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Anil Ahlawat
Editor

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CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

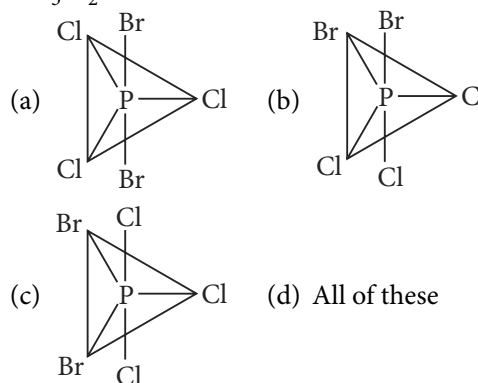
PROBLEM Set 27

JEE MAIN/PMTs

- It is easier to liquify oxygen than hydrogen because
 - oxygen has higher T_c and lower inversion temperature (T_i) than hydrogen
 - oxygen has lower T_c and higher T_i than hydrogen
 - oxygen has higher T_c and T_i than hydrogen
 - oxygen has lower T_c and T_i than hydrogen.
- Which is the most effective procedure for removing triethylamine from a solution of triethylammonium hydrogen sulphate in water?
 - Add NaOH then extract with benzene
 - Add HCl then extract with benzene
 - Add HCl then extract with pyridine
 - None of these
- The red line for the lithium in the Bunsen burner flame arises due to the formation of
 - Li^+ ion
 - LiOH
 - Li_2O
 - Li^{2+} ion.
- When solid CaCl_2 is added to liquid water, the temperature rises. When solid CaCl_2 is added to ice at 0°C , then
 - temperature increases
 - temperature decreases
 - temperature remains same
 - temperature may increase or decrease.
- 0.001 mol of $\text{Cr}(\text{NH}_3)_5(\text{NO}_3)(\text{SO}_4)$ was passed through cation exchanger and the acid coming out required 20 mL of 0.1 M NaOH for neutralisation. Hence the complex is
 - $[\text{Cr}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$
 - $[\text{Cr}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$
 - $[\text{Cr}(\text{NH}_3)_4(\text{NO}_3)(\text{SO}_4)]\text{NH}_3$
 - $[\text{Cr}(\text{NH}_3)_5](\text{NO}_3)(\text{SO}_4)$

JEE ADVANCED

- Which of the following is correct structure of PCl_3Br_2 ?

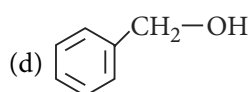
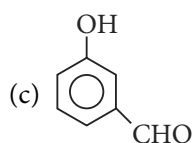
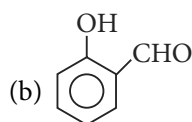
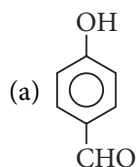


COMPREHENSION

An organic compound (A) gives positive Liebermann nitroso reaction and on treatment with CHCl_3/KOH followed by hydrolysis gives (B) and (C). Compound (B) gives pink colour with

Schiff's reagent but not (C) which is steam volatile. (C) on treatment with LiAlH_4 gives (D) ($\text{C}_7\text{H}_8\text{O}_2$) which on oxidation gives (E). (E) reacts with acetic anhydride and gives compound (F).

7. The compound (B) is

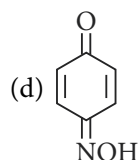


8. In the Liebermann nitroso reaction the compound formed is _____ which gives red colour with phenol.

(a) aspirin

(b) salicylic acid

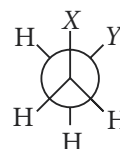
(c) azo dye of phenol



INTEGER VALUE

9. The pH of an aqueous solution of NH_4Cl is given by the equation $\text{pH} = 2.5 - \log \sqrt{C}$. The value of $\text{p}K_b$ for weak base is

10. The Newmann's structure of a compound is given as



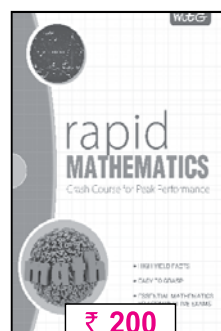
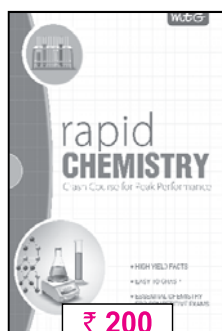
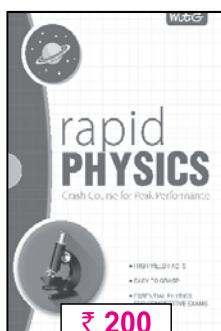
In how many combinations of X and Y the gauche form is more stable than anti?

- CH_3, OH
- OH, F
- NH_2, OH
- NH_2, CH_3
- F, NH_2
- F, CH_3
- CH_3, CH_3
- H, H

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EXAMINER'S MIND

CLASS XI



The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI. This year JEE (Main & Advanced)/AIPMT/AIIMS/other PMTs have drawn their papers heavily from NCERT books.

EQUILIBRIUM | REDOX REACTIONS

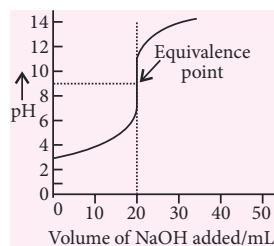
SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- In the reaction, $A_{2(g)} + 4B_{2(g)} \rightleftharpoons 2AB_{4(g)}$, $\Delta H < 0$
The formation of AB_4 will be favoured at
(a) low temperature, high pressure
(b) high temperature, low pressure
(c) low temperature, low pressure
(d) high temperature, high pressure.
- A compound contains atoms X, Y, Z. The oxidation number of X is +2, Y is +5, and Z is -2. The possible formula of the compound is
(a) XY_1Z_2 (b) $Y_2(XZ_3)_2$
(c) $X_3(YZ_4)_2$ (d) $X_3(Y_4Z)_2$
- At temperature T , a compound $AB_{2(g)}$ dissociates according to the reaction : $2AB_{2(g)} \rightleftharpoons 2AB_{(g)} + B_{2(g)}$ with a degree of dissociation 'x' which is small compared to unity. Expression for x is
(a) $\sqrt[4]{\frac{2K_p}{P}}$ (b) $\sqrt[3]{\frac{2K_p}{P}}$
(c) $\sqrt{\frac{2K_p}{9P}}$ (d) $\sqrt{K_p}$
- Which of the following is not a redox reaction?
(a) $CaCO_3 \longrightarrow CaO + CO_2$
(b) $Na + H_2O \longrightarrow NaOH + \frac{1}{2} H_2$
(c) $MnCl_3 \longrightarrow MnCl_2 + \frac{1}{2} Cl_2$
(d) $O_2 + 2H_2 \longrightarrow 2H_2O$
- Solubility of Ag_2CrO_4 is decreased in presence of
(a) $AgNO_3$ (b) $AgCl$
(c) $BaCrO_4$ (d) $PbCrO_4$
- What volume of 0.01 M $K_2Cr_2O_7$ would be required to oxidise Fe (II) in 50 mL of 0.03 M solution of ferrous ammonium sulphate in acidic medium?
(a) 150 mL (b) 75 mL
(c) 50 mL (d) 25 mL
- The pH value of 10^{-8} M HCl is
(a) more than 7 (b) less than 7
(c) equal to 7 (d) either (a) or (c).
- The colour of $K_2Cr_2O_7$ changes from red-orange to lemon-yellow on treatment with $KOH_{(aq)}$, because of
(a) reduction of Cr (VI) to Cr (III)
(b) formation of chromium hydroxide
(c) conversion of dichromate into chromate ion
(d) oxidation of potassium hydroxide to potassium peroxide.
- Ice and water are placed in a closed container at a pressure of 1 atm and temperature 273.15 K. If pressure of the system is increased to 2 atm while keeping temperature constant, which of the following would be the correct observation?
(a) The liquid phase disappears completely.
(b) The amount of ice decreases.
(c) The solid phase (ice) disappears completely.
(d) Volume of the system increases.
- Which of the following statements is not correct?
(a) The oxidation number of S in $(NH_4)_2S_2O_8$ is +6.
(b) The oxidation number of Os in OsO_4 is +8.
(c) The oxidation number of S in H_2SO_5 is +8.
(d) The oxidation number of O in KO_2 is -1/2.

11. Following is the titration curve of CH_3COOH against NaOH added with phenolphthalein as the indicator.



K_{In} value of phenolphthalein is 4.0×10^{-10} .

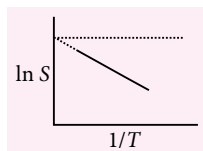
Choose the incorrect statement.

- (a) It begins to change colour from the pH 9.4.
 (b) It begins to change colour from acid (colourless) at pH 8.4 to the base form (reddish pink) at pH 10.4.
 (c) Phenolphthalein is suitable indicator for $\text{CH}_3\text{COOH} - \text{NaOH}$ titration.
 (d) Phenolphthalein is a weak acid.
12. When a piece of copper wire is immersed in a solution of aqueous silver nitrate, the solution becomes blue. This is a consequence of
 (a) oxidation of silver
 (b) oxidation of copper
 (c) formation of a copper complex
 (d) reduction of copper.
13. The $\text{p}K_a$ of acetylsalicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2-3 and the pH in the small intestine is about 8. Aspirin will be
 (a) unionised in the small intestine and in the stomach
 (b) completely ionised in the small intestine and in the stomach
 (c) ionised in the stomach and almost unionised in the small intestine
 (d) ionised in the small intestine and almost unionised in the stomach.
14. Values of p , q , r , s and t in the following redox reaction are respectively
 $p\text{Br}_2 + q\text{OH}^- \longrightarrow r\text{Br}^- + s\text{BrO}_3^- + t\text{H}_2\text{O}$
 (a) 3, 6, 1, 5 and 3 (b) 3, 6, 5, 3 and 1
 (c) 3, 6, 5, 1 and 3 (d) 3, 5, 1, 6 and 3
15. A weak acid HA has degree of dissociation x . Thus $(\text{pH} - \text{p}K_a)$ is
 (a) $\log(1 + 2x)$ (b) $\log\left(\frac{1-x}{x}\right)$
 (c) 0 (d) $\log\left(\frac{x}{1-x}\right)$
16. The complex $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ is formed in the ring test for nitrate ion (NO_3^-) when freshly prepared FeSO_4 solution is added to aqueous solution of

NO_3^- followed by the addition of conc. H_2SO_4 . This complex is formed by charge transfer in which

- (a) Fe^{2+} changes to Fe^{3+} and NO^+ changes to NO
 (b) Fe^{2+} changes to Fe^{3+} and NO changes to NO^+
 (c) Fe^{2+} changes to Fe^+ and NO changes to NO^+
 (d) none of these.

17. The solubility of a solute in water varies with temperature as given by: $S = A e^{-\Delta H/RT}$, ΔH being the enthalpy of solution.



For a given solute, variation of $\ln S$ with temperature is as shown in the figure. The solute is expected to be

- (a) CaO (b) CuSO_4
 (c) MgSO_4 (d) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
18. Ratio of moles of Fe(II) oxidised by equal volumes of equimolar KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ solutions in acidic medium will be
 (a) 5 : 3 (b) 1 : 1 (c) 1 : 2 (d) 5 : 6
19. The correctly balanced net ionic equation for the reaction that occurs when a solution of acetic acid is mixed with a solution of sodium carbonate is :
 (a) $\text{CH}_3\text{COOH}_{(aq)} + \text{CO}_3^{2-}_{(aq)} \rightleftharpoons \text{CH}_3\text{COO}^-_{(aq)} + \text{HCO}_3^-_{(aq)}$
 (b) $\text{H}_3\text{O}^+_{(aq)} + \text{CO}_3^{2-}_{(aq)} \rightleftharpoons \text{HCO}_3^-_{(aq)} + \text{H}_2\text{O}_{(l)}$
 (c) $\text{CH}_3\text{COOH}_{(aq)} + \text{Na}_2\text{CO}_3_{(aq)} \rightleftharpoons \text{CH}_3\text{COO}^-_{(aq)} + \text{NaHCO}_3_{(aq)} + \text{Na}^+_{(aq)}$
 (d) $\text{CH}_3\text{COOH}_{(aq)} + \text{OH}^-_{(aq)} \rightleftharpoons \text{CH}_3\text{COO}^-_{(aq)} + \text{H}_2\text{O}_{(l)}$
20. The standard reduction potential values of three metallic cations, X , Y and Z are 0.52, -3.03 and -1.18 V respectively. The order of reducing power of the corresponding metals is
 (a) $Y > Z > X$ (b) $X > Y > Z$
 (c) $Z > Y > X$ (d) $Z > X > Y$

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

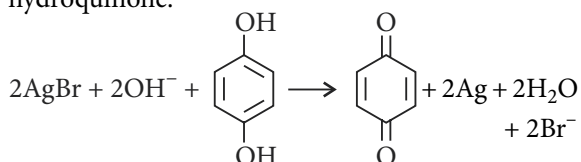
21. pH of following solution is not affected by dilution
 (a) 0.01 M $\text{CH}_3\text{COONH}_4$ (b) 0.01 M NaH_2PO_4
 (c) 0.01 M NaCl (d) 0.01 M NaHCO_3
22. Which of the following statements is/are correct? In the reaction
 $x\text{Cu}_3\text{P} + y\text{Cr}_2\text{O}_7^{2-} \longrightarrow \text{Cu}^{2+} + \text{H}_3\text{PO}_4 + \text{Cr}^{3+}$

- (a) Cu in Cu_3P is oxidised to Cu^{2+} and P in Cu_3P is also oxidised to PO_4^{3-}
 (b) Cu in Cu_3P is oxidised to Cu^{2+} whereas P in Cu_3P is reduced to H_3PO_4
 (c) 11 electrons are involved in the conversion of Cu_3P to Cu^{2+} and H_3PO_4
 (d) the value of x is 6.

23. In the presence of a catalyst, what happens to the chemical equilibrium?

- (a) Energy of activation of the forward and backward reactions is lowered by same amount.
 (b) Equilibrium amount is not disturbed.
 (c) Rates of forward and reverse reactions increase by the same factor.
 (d) More product is formed.

24. Photographic paper is developed with alkaline hydroquinone.



Select the correct statement.

- (a) Hydroquinone is the oxidant.
 (b) Ag^+ is the oxidant.
 (c) Br^- is the oxidant.
 (d) Ag^+ is the reductant.
25. 138 g of $\text{N}_2\text{O}_{4(g)}$ is placed in 8.2 L container at 300 K. The equilibrium vapour density of mixture was found to be 30.67. Then ($R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$)
 (a) the total pressure at equilibrium = 4.5 atm
 (b) the degree of dissociation of $\text{N}_2\text{O}_5 = 0.25$
 (c) the total number of moles at equilibrium is 1.5
 (d) K_p of $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_{2(g)}$ will be 6 atm.

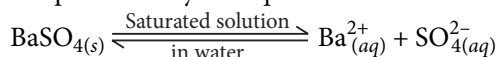
SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

A solid like barium sulphate is in contact with its saturated aqueous solution. The equilibrium between the undissolved solid and the ions in a saturated solution can be represented by the equation :



The equilibrium constant is given by the equation :

$$K = \{[\text{Ba}^{2+}][\text{SO}_4^{2-}]\} / [\text{BaSO}_4]$$

For a pure solid substance the concentration remains constant and we can write

$$K_{sp} = K[\text{BaSO}_4] = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

We call K_{sp} the solubility product constant or simply solubility product. The experimental value of K_{sp} in above equation at 298 K is 1.1×10^{-10} . This means that for solid barium sulphate in equilibrium with its saturated solution, the product of the concentration of barium and sulphate ions is equal to its solubility product constant. The concentrations of the two ions will be equal to the molar solubility of the barium sulphate.

26. At 25°C the solubility of calcium phosphate (molecular weight = M) was found to be w g/100 mL. The K_{sp} for calcium phosphate at 25°C is approximately

- (a) $10^2 \left(\frac{w}{M} \right)^5$ (b) $10^4 \left(\frac{w}{M} \right)^5$
 (c) $10^7 \left(\frac{w}{M} \right)^5$ (d) $10^9 \left(\frac{w}{M} \right)^5$

27. The solubility product (K_{sp}) of a sparingly soluble salt MX at 25°C is 2.5×10^{-9} . The solubility of salt (in mol L^{-1}) at 25°C is

- (a) 1×10^{-14} (b) 5.0×10^{-8}
 (c) 1.25×10^{-9} (d) 5.0×10^{-5}

28. The K_{sp} of AgCl is 4.0×10^{-10} at 298 K. The solubility of AgCl in 0.04 M CaCl_2 will be

- (a) $2.0 \times 10^{-5} \text{ M}$ (b) $10 \times 10^{-4} \text{ M}$
 (c) $5.0 \times 10^{-9} \text{ M}$ (d) $2.2 \times 10^{-4} \text{ M}$

Paragraph for Questions 29 to 31

In redox systems, the titration method can be adopted to determine the strength of a reductant/ oxidant using a redox sensitive indicator. The usage of indicators in redox titration is illustrated below :

In one situation, the reagent itself is intensely coloured, e.g., permanganate ion, MnO_4^- acts as the self indicator. If there is no dramatic auto-colour change (as with MnO_4^- titration), there are indicators which are oxidised immediately after the last bit of the reactant is consumed, producing a dramatic colour change. The best example is afforded by $\text{Cr}_2\text{O}_7^{2-}$, which is not a self-indicator, but oxidises the indicator substance diphenylamine just after the equivalence point to produce an intense blue colour, thus signalling the end point.

29. What suitable substance and its amount will be needed to prepare 100 mL of 0.1 N standard solution for the estimation of KMnO_4 solution?

- (a) Oxalic acid sample, 0.6300 g
 (b) Oxalic acid sample, 0.9000 g
 (c) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 2.805 g
 (d) Mohr's salt, 3.9200 g

30. How can the concentration of NaOH solution be determined?

- (a) By titrating it with oxalic acid solution prepared from the given sample.
 (b) By titrating it with acetic acid solution prepared from the given sample.
 (c) By titrating it with oxalic acid solution standardised by KMnO_4 solution.
 (d) By titrating it with acetic acid solution standardised by KMnO_4 solution.

31. What is the final product of Mn in the redox reaction of oxalic acid with KMnO_4 in acidic medium?

- (a) MnO_4^{2-} (b) MnO_2
 (c) Mn^{2+} (d) Mn_2O_3

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

32. Match the change of pressure and temperature in List I with the reaction in List II and select the correct answer using the code given below the lists:

- | List I | | List II | |
|---------------------|---|---------|--|
| P. P is increased | 1. Solubility of KCl in H_2O is increased | | |
| Q. P is decreased | 2. Solubility of gas in H_2O is increased | | |
| R. T is increased | 3. Dissociation of PCl_5 is increased | | |
| S. T is decreased | 4. Exothermic reaction is in forward side. | | |

- | | P | Q | R | S |
|-----|---|---|---|---|
| (a) | 4 | 3 | 1 | 2 |
| (b) | 2 | 3 | 1 | 4 |
| (c) | 2 | 4 | 3 | 1 |
| (d) | 1 | 2 | 3 | 4 |

33. Given two mixtures : (I) NaOH and Na_2CO_3 and (II) NaHCO_3 and Na_2CO_3 .
 100 mL of mixture I required w and x mL of 1 M HCl in separate titrations using phenolphthalein and methyl orange indicators while 100 mL of mixture II required y and z mL of same HCl solution in separate titrations using the same indicators.

Match the List I with List II and select the correct answer using code given below the lists :

- | List I | | List II | |
|---|--------------------------------|---------|--|
| P. Na_2CO_3 in mixture I | 1. $(2w - x) \times 10^{-2}$ M | | |
| Q. Na_2CO_3 in mixture II | 2. $(z - 2y) \times 10^{-2}$ M | | |
| R. NaOH in mixture I | 3. $y \times 10^{-2}$ M | | |
| S. NaHCO_3 in mixture II | 4. $(x - w) \times 10^{-2}$ M | | |
- | | P | Q | R | S |
|-----|---|---|---|---|
| (a) | 1 | 3 | 3 | 4 |
| (b) | 4 | 3 | 2 | 1 |
| (c) | 4 | 3 | 1 | 2 |
| (d) | 1 | 4 | 3 | 2 |

34. Match the processes mentioned in List I with the characteristics listed in List II and select the correct answer using the code given below the lists :

- | List I | | List II | |
|--|---|---------|--|
| P. $2\text{N}_2\text{O}_{(g)} \longrightarrow 2\text{N}_{2(g)} + \text{O}_{2(g)} + 2 \text{ kJ}$ | 1. Spontaneous at low temperature but non-spontaneous at high temperature | | |
| Q. $\text{H}_2\text{O}_{(g)} \longrightarrow \text{H}_2\text{O}_{(l)}$ | 2. Spontaneous at high temperature and non-spontaneous at low temperature | | |
| R. $2\text{NH}_3_{(g)} + 2 \text{ kJ} \longrightarrow \text{N}_{2(g)} + 3\text{H}_{2(g)}$ | 3. Non-spontaneous at all temperatures | | |
| S. $3\text{O}_{2(g)} + 2 \text{ kJ} \longrightarrow 2\text{O}_{3(g)}$ | 4. Spontaneous at all temperatures | | |
- | | P | Q | R | S |
|-----|---|---|---|---|
| (a) | 1 | 4 | 2 | 3 |
| (b) | 4 | 1 | 2 | 3 |
| (c) | 3 | 2 | 1 | 4 |
| (d) | 4 | 3 | 2 | 1 |

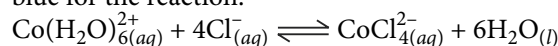
SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

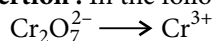
- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
 (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
 (c) If assertion is true but reason is false.
 (d) If both assertion and reason are false.

35. **Assertion :** On cooling in a freezing mixture, colour of the following mixture turns to pink from deep blue for the reaction.



Reason : Reaction is endothermic. So on cooling, the reaction moves to backward direction.

36. **Assertion :** In the following half reaction :



Equivalent weight of $\text{Cr}_2\text{O}_7^{2-} = \frac{\text{Molar mass}}{3}$

Reason : Change in oxidation number of chromium is 3 per atom.

37. **Assertion :** Aqueous solution of ammonium carbonate is basic.

Reason : Acidic or basic nature of a salt solution of a salt of weak acid and weak base depends on K_a and K_b value of the acid and the base forming it.

38. **Assertion :** Lithium ion is a poor oxidising agent.

Reason : Lithium ion has the lowest electrode potential.

39. **Assertion :** If Q_c (reaction quotient) $< K_c$ (equilibrium constant) reaction moves in direction of reactants.

Reason : Reaction quotient is defined in the same way as equilibrium constant at any stage of the reaction.

40. **Assertion :** The decomposition of hydrogen peroxide to form water and oxygen is an example of disproportionation reaction.

Reason : The oxygen of peroxide is in -1 oxidation state and it is converted to zero oxidation state in O_2 and -2 oxidation state in H_2O .

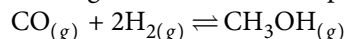
SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. Difference in oxidation number of two Cl atoms in bleaching powder is

42. 0.20 mole of CO was taken in a 2.50 L flask maintained at 750 K along with a catalyst so that the following reaction could take place :



Hydrogen was introduced until the total pressure in the flask at equilibrium was 12.30 atm and 0.10 mole of CH_3OH was formed. The equilibrium constant is 1.83×10^{-x} . The value of x is

43. A 1.0 g of sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made up to 100.00 mL. An aliquot of 25.0 mL of this solution requires 17.0 mL of 0.0167 M solution of an oxidant for titration. The number of

electrons taken up by the oxidant in the reaction of the above titration is (mol. wt. of $\text{Fe}_2\text{O}_3 = 160$)

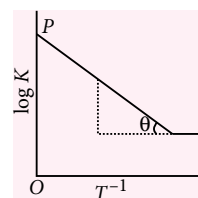
44. 0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. The H^+ concentration in the solution is $x \times 10^{-y}$. The value of x is

45. If the following is balanced reaction, $4\text{O}_2^{x-} + 2\text{H}_2\text{O} \longrightarrow 4\text{OH}^- + 3\text{O}_2$ then x is

46. Variation of equilibrium constant K with temperature T is given by van't Hoff equation

$$\log K = \log A - \frac{\Delta H^\circ}{2.303 RT}$$

A graph between $\log K$ and T^{-1} was a straight line as shown in figure and having



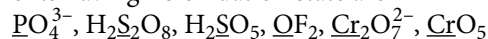
$$\theta = \tan^{-1}(0.5) \text{ and } OP = 10.$$

The equilibrium constant K at 298 K is 9.96×10^x . The value of x is

47. 2.496×10^{-x} g of pyrolusite containing 89.21% of MnO_2 will oxidise the same amount of oxalic acid as 37.12 mL of permanganate solution one mL of which, liberates 0.0175 g of I_2 from KI. The value of x is

48. An acid type indicator, HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio $[\text{In}^-]/[\text{HIn}]$ is greater than 10 or smaller than 0.1. Minimum change in the pH of the solution to observe a complete colour change is ($K_a = 1.0 \times 10^{-5}$)

49. Among the following, the number of underlined elements having +6 oxidation state are

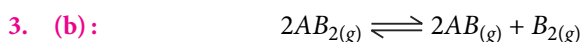


50. 1 mol of N_2H_4 loses 10 mol of electrons to form a new compound Y. Assuming that all the nitrogen appear in the new compound, the oxidation state of nitrogen in Y (no change in the oxidation state of H) is

SOLUTIONS

1. (a) : Since, the reaction is exothermic (as $\Delta H < 0$), low temperature favours forward reaction. Moreover $n_P < n_R$, high pressure favours forward reaction.

2. (c) : Sum of oxidation number of all the atoms in a neutral compound must be equal to zero.



Moles before dissociation	1	0	0
Moles after dissociation	$(1-x)$	x	$\frac{x}{2}$

$$\text{Total moles at equilibrium } (\Sigma n) = 1 - x + x + \frac{x}{2} = 1 + \frac{x}{2}$$

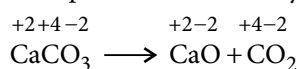
$$\text{Now, } K_p = \frac{n_{B_2} \times (n_{AB})^2}{(n_{AB_2})^2} \times \left[\frac{P}{\Sigma n} \right]^{\Delta n}$$

$$K_p = \frac{\frac{x}{2} \cdot (x)^2}{(1-x)^2} \times \left[\frac{P}{1 + \frac{x}{2}} \right]^1$$

$$K_p = \frac{x^3 P}{2} \left[\because x \text{ is small, } \therefore 1-x \approx 1 \text{ and } 1 + \frac{x}{2} \approx 1 \right]$$

$$\text{or } x = \sqrt[3]{\frac{2K_p}{P}}$$

4. (a) : In redox reaction, oxidation and reduction takes place simultaneously.



Since, in this reaction, no oxidation or reduction take place thus, it is not a redox reaction.

5. (a) : AgCl, BaCrO₄, PbCrO₄ are sparingly soluble salts hence, are not effective in decreasing solubility of Ag₂CrO₄.

6. (d) : Fe (II) \rightarrow Fe (III) + e^- , 'n' factor = 1;
 $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$, 'n' factor = 6
Hence, $6 \times 0.01 \times V = 1 \times 0.03 \times 50 \Rightarrow V = 25 \text{ mL}$

7. (b) : When H^+ conc. of acid is less than H_2O then H^+ conc. of water cannot be neglected.

$$\therefore [\text{H}^+] = 10^{-8} + 10^{-7} = 10^{-7} (0.1 + 1) = 1.1 \times 10^{-7}$$

$$\therefore \text{pH} = -\log(1.1 \times 10^{-7}) = 7 - \log 1.1 = 6.96$$

8. (c) : $\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{KOH} \longrightarrow 2\text{K}_2\text{CrO}_4 + \text{H}_2\text{O}$
(Red-orange) (Lemon-yellow)

9. (c) : Ice \rightleftharpoons water at $P = 1 \text{ atm}$ and $T = 273.15 \text{ K}$
For $P > 1 \text{ atm}$ and $T = 273.15 \text{ K}$ equilibrium shifts completely in forward direction leading to reduction in volume of the system. i.e., ice melts completely.

10. (c) : $(\text{NH}_4)_2\text{S}_2\text{O}_8$
 \therefore Oxidation state of S = +6
(Since $\text{S}_2\text{O}_8^{2-}$ has one peroxide bond)

- (b) Oxidation state of Os in $\text{OsO}_4 = +8$

- (c) Oxidation state of S in $\text{H}_2\text{SO}_5 = +6$

(Since it has one peroxide bond)

- (d) $\text{K}^+\text{O}_2^{1-}$ oxidation state of O = $-1/2$

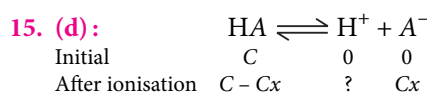
11. (a) : $\text{p}K_{\text{In}} = -\log K_{\text{In}} = 10 - \log 4 = 9.4$

Thus, it is the equivalence point. pH colour change starts from $(\text{p}K_{\text{In}} - 1)$ and completes at $(\text{p}K_{\text{In}} + 1)$.

12. (b) : Solution turns blue due to oxidation of Cu to Cu^{2+} ions in the solution.

13. (d) : Aspirin a weak acid is unionised in acidic medium due to common ion effect and completely ionised in alkaline medium.

14. (c)



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]} = K_a \frac{C(1-x)}{Cx} = K_a \left(\frac{1-x}{x} \right)$$

$$\log [\text{H}^+] = \log K_a + \log (1-x) - \log x$$

$$-\log [\text{H}^+] = -\log K_a - \log (1-x) - (-\log x)$$

$$\text{pH} = \text{p}K_a - \log(1-x) + \log x$$

$$\text{pH} - \text{p}K_a = \log \left(\frac{x}{1-x} \right)$$

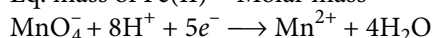
16. (c) : $\text{Fe}^{2+} + e^- \longrightarrow \text{Fe}^+$
 $\text{NO} \longrightarrow \text{NO}^+ + e^-$

17. (d) : $\ln S = \ln A - \frac{\Delta H}{R} \times \frac{1}{T}$

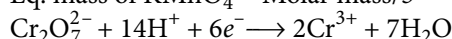
The slope of the graph is negative, so $\Delta H > 0$ i.e., the process is endothermic. Dissolution of hydrated salts is an endothermic process.

18. (d) : $\text{Fe(II)} \longrightarrow \text{Fe(III)} + e^-$

Eq. mass of Fe(II) = Molar mass



Eq. mass of KMnO_4 = Molar mass/5



Eq. mass of $\text{K}_2\text{Cr}_2\text{O}_7$ = Molar mass/6

Eq. of KMnO_4 in V L of x M = $5xV$ = Mol of Fe (II) oxidised by KMnO_4

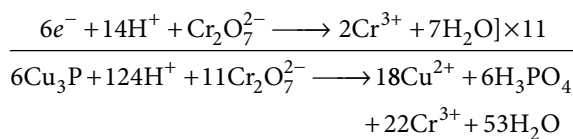
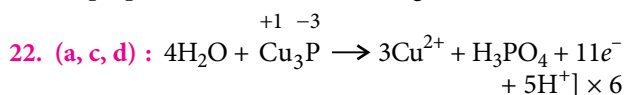
Eq. of $\text{K}_2\text{Cr}_2\text{O}_7$ in V L of x M = $6xV$ = Mol of Fe (II) oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$

Hence, ratio of moles of Fe (II) oxidised by KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7 = 5 : 6$

19. (d) : Na_2CO_3 solution is alkaline due to hydrolysis
 $\text{CO}_3^{2-} + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + 2\text{OH}^-$
 OH^- neutralises CH_3COOH .

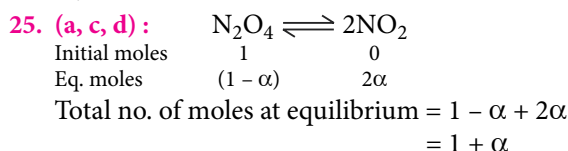
20. (a) : More negative or lower the reduction potential, more is the reducing property. Thus, the order of reducing power is $Y > Z > X$.

21. (a, b, d) : In aqueous solution, a salt of weak acid and a weak base acts as a buffer solution. The pH of a buffer solution do not change on dilution. Thus, pH of 0.01 M $\text{CH}_3\text{COONH}_4$ will not change on dilution. NaHCO_3 and H_2PO_4^- from NaH_2PO_4 are amphiprotic anions. The pH of solution containing amphiprotic anions do not change on dilution.



23. (a, b, c)

24. (b) : Ag^+ is reduced hence, it is an oxidant. Hydroquinone is oxidised hence, it is a reductant.



$$\alpha = \frac{1}{n-1} \left(\frac{D-d}{d} \right)$$

where, D = Theoretical vapour density

$$= \frac{\text{Mol. mass}}{2} = \frac{92}{2} = 46$$

d = Observed vapour density

n = No. of moles of products formed from the dissociation of 1 mole of N_2O_4

$$\therefore \alpha = \frac{1}{2-1} \left(\frac{46-30.67}{30.67} \right) = 0.4998 \approx 0.5$$

Thus, total no. of moles at equilibrium = $1 + 0.5 = 1.5$

$$\text{Total pressure} = \frac{1.5 \times 0.082 \times 300}{8.2} = 4.5 \text{ atm}$$

$$\text{So, } K_p = \frac{4\alpha^2}{1-\alpha^2} \times 4.5 = 6 \text{ atm}$$

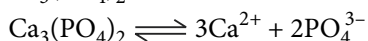
26. (c) : Given solubility of calcium phosphate at 25°C

$$= w \text{ g/100 mL} = 10 w \text{ g/1000 mL}$$

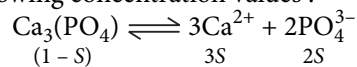
$$= 10 w \text{ g/L}$$

$$= \frac{10w}{M} \text{ mol/L (Molecular weight = } M\text{)}$$

$\text{Ca}_3(\text{PO}_4)_2$ ionises in water as :



If solubility is 'S' then at equilibrium, we have the following concentration values :



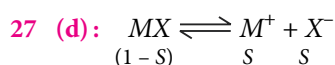
$$\text{Thus } K_{sp} = (3S)^3 \times (2S)^2 = 27S^3 \times 4S^2 = 108 S^5$$

Since the solubility of calcium phosphate at 25°C

$$= \left(\frac{10w}{M} \right)$$

$$\text{We get, } K_{sp} = 108 \times \left(\frac{10w}{M} \right)^5$$

$$= 1.08 \times 10^7 \times \left(\frac{w}{M} \right)^5 \approx 1 \times 10^7 \times \left(\frac{w}{M} \right)^5$$

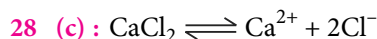


$$K_{sp} = S^2$$

$$\text{or } S = \sqrt{K_{sp}}$$

$$= \sqrt{2.5 \times 10^{-9}} = \sqrt{25 \times 10^{-10}}$$

$$\text{or } 5.0 \times 10^{-5} \text{ mol L}^{-1}$$



CaCl_2 is a strong electrolyte and may be considered as completely ionised at 25°C .

$$\therefore [\text{Cl}^-] \text{ in } 0.04 \text{ M } \text{CaCl}_2 = 2 \times 0.04 = 0.08 \text{ M}$$

Let solubility of AgCl in 0.04 M CaCl_2 be S . Thus,

$$[\text{Ag}^+] = [\text{Cl}^-] = S \text{ mole l}^{-1} \quad [\text{From AgCl}]$$

$$\therefore \text{Total } [\text{Cl}^-] = 0.08 + S \approx 0.08 \text{ M}$$

$$K_{sp} = [\text{Ag}^+] [\text{Cl}^-] = 4.0 \times 10^{-10}$$

$$S \times 0.08 = 4.0 \times 10^{-10}$$

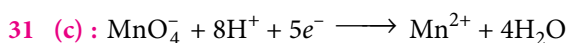
$$\therefore S[\text{Ag}^+] = \frac{4.0 \times 10^{-10}}{0.08} = 5.0 \times 10^{-9} \text{ M}$$

29. (d) : Although oxalic acid is oxidised by KMnO_4 in acidic medium, it cannot be used to prepare the standard solution because the sample is impure. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is not a substance of primary standard because it gets oxidised by atmospheric oxygen and its composition is not known. Mohr's salt, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ is not prone to oxidation by atmospheric oxygen and is a substance of primary standard, and can be used to prepare a standard solution of Fe (II) which reduces acidified KMnO_4 .

Mass of Mohr's salt required

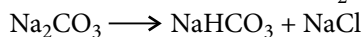
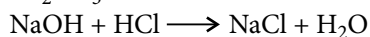
$$= \frac{392 \times 0.1 \times 100}{1000} = 3.92 \text{ g}$$

30. (c) : Both oxalic acid and acetic acid samples can not be used to prepare standard solutions. Acetic acid solution cannot be standardised by KMnO_4 solution as acetic acid does not reduce KMnO_4 .

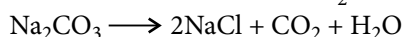
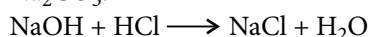


32 (b)

33. (c) : **Mixture I** : End point with phenolphthalein (disappearance of pink colour) corresponds to neutralisation of NaOH and half neutralisation of Na_2CO_3 .



End point with methyl orange (appearance of red colour) corresponds to neutralisation of NaOH and Na_2CO_3 .



Volume of HCl required for neutralisation of $\text{Na}_2\text{CO}_3 = 2(x - w)$ mL

$$\begin{aligned}\text{Normality of } \text{Na}_2\text{CO}_3 &= \frac{1 \times 2(x - w)}{100} \\ &= 2(x - w) \times 10^{-2} \text{ N}\end{aligned}$$

$$\text{Molarity of } \text{Na}_2\text{CO}_3 = (x - w) \times 10^{-2} \text{ M}$$

Volume of HCl required for neutralisation of

$$\text{NaOH} = w - (x - w) = 2w - x \text{ mL}$$

$$\begin{aligned}\text{Hence, molarity of NaOH} &= \frac{1 \times (2w - x)}{100} \\ &= (2w - x) \times 10^{-2} \text{ M}\end{aligned}$$

Mixture II : End point with phenolphthalein corresponds to half neutralisation of Na_2CO_3 as :



Volume of HCl needed for complete neutralisation of $\text{Na}_2\text{CO}_3 = 2y$

$$\begin{aligned}\text{Hence, molarity of } \text{Na}_2\text{CO}_3 &= \frac{1}{2} \times \frac{1 \times 2y}{100} \\ &= y \times 10^{-2} \text{ M}\end{aligned}$$

End point with methyl orange corresponds to neutralisations of NaHCO_3 already present and that formed from Na_2CO_3 .

Hence, volume required for neutralisation of NaHCO_3 present initially $= z - 2y$

$$\begin{aligned}\text{Hence, molarity of } \text{NaHCO}_3 &= \frac{1 \times (z - 2y)}{100} \\ &= (z - 2y) \times 10^{-2} \text{ M}\end{aligned}$$

34. (b) : (P) $\Delta H < 0$ and $\Delta S > 0$. Hence $\Delta G = \Delta H - T\Delta S$ will be negative at all temperatures.

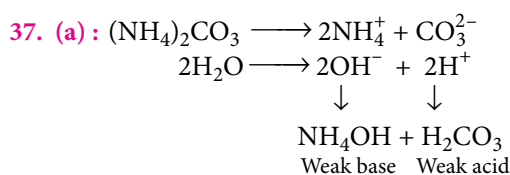
(Q) $\Delta H < 0$ and $\Delta S < 0$. ΔG would be positive at high temperatures and negative at low temperatures.

(R) $\Delta H > 0$ and $\Delta S > 0$. ΔG would be negative at high temperatures and positive at low temperatures.

(S) $\Delta H > 0$ and $\Delta S < 0$. ΔG would be positive at all temperatures. Both energy and entropy factors oppose the process.

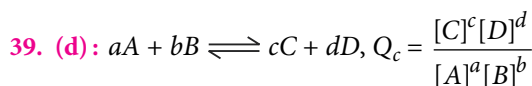
35. (a) : $\text{Co}(\text{H}_2\text{O})_6^{2+}$ is pink while CoCl_4^{2-} is blue. So, on cooling the reaction tries to overcome the effect of temperature and goes in backward direction (Le-Chatelier's principle).

$$36. (d) : \text{Equivalent weight of } \text{Cr}_2\text{O}_7^{2-} = \frac{\text{Molar mass}}{6}$$



As K_b of $\text{NH}_4\text{OH} > K_a$ of H_2CO_3 , the solution is basic.

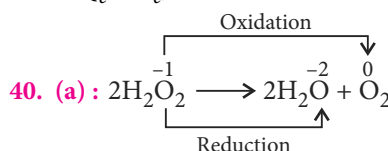
38. (a) : Greater the standard electrode potential powerful is the oxidising agent while lower the electrode potential weaker is the oxidising agent.



If $Q_c > K_c$, reaction will proceed in the direction of reactants.

If $Q_c < K_c$, reaction will move in the direction of products.

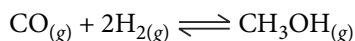
If $Q_c = K_c$, the reaction mixture is at equilibrium.



41. (2) : Bleaching powder is CaOCl_2 . Oxidation states of two Cl atoms in CaOCl_2 are -1 and +1.

42. (2) : Moles of all gases at equilibrium

$$n = \frac{PV}{RT} = \frac{12.30 \times 2.5}{0.082 \times 750} = 0.5$$



Moles of CH_3OH at equilibrium = 0.10

Moles of CO at equilibrium = $0.20 - 0.10 = 0.10$

Moles of H_2 at equilibrium = $0.5 - (0.10 + 0.10) = 0.30$

Partial pressure of $\text{CH}_3\text{OH} = x_{\text{CH}_3\text{OH}} P$

$$= \frac{0.1}{0.5} \times 12.3 \text{ atm} = 2.46 \text{ atm}$$

Partial pressure of CO = $x_{\text{CO}} P$

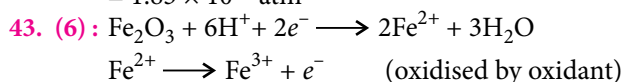
$$= \frac{0.1}{0.5} \times 12.3 = 2.46 \text{ atm}$$

Partial pressure of $\text{H}_2 = x_{\text{H}_2} P$

$$= \frac{0.3}{0.5} \times 12.3 = 7.38 \text{ atm}$$

$$K_p = \frac{p_{\text{CH}_3\text{OH}}}{p_{\text{CO}} \times p_{\text{H}_2}^2} = \frac{2.46}{2.46 \times (7.38)^2}$$

$$= 1.83 \times 10^{-2} \text{ atm}^{-2}$$



$$\text{Mass of Fe}_2\text{O}_3 \text{ in the sample} = \frac{55.2}{100} = 0.552 \text{ g}$$

$$\text{Equivalent mass of Fe}_2\text{O}_3 = \frac{160}{2} = 80$$

$$\text{Number of milliequivalents of Fe}_2\text{O}_3 = \frac{0.552 \times 10^3}{80}$$

$$= 6.9$$

Let n electrons be taken up by 1 mole of oxidant.

Then, Normality = $n \times$ molarity

Normality of oxidant solution = $0.0167 \times n$

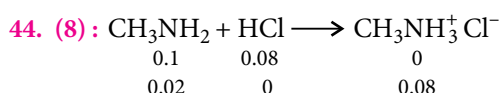
Milliequivalents of oxidant used up

$$= \frac{17 \times 0.0167 \times n \times 100}{25} = 1.1356 n$$

$$\text{Meq. of Fe}_2\text{O}_3 = \text{Meq. of Fe}^{2+} \text{ formed}$$

$$= \text{Meq. of oxidant}$$

$$\text{Hence } 1.1356 n = 6.9 \Rightarrow n = 6.07 \approx 6$$



As it is a basic buffer solution.

$$\text{pOH} = \text{p}K_b + \log \frac{0.08}{0.02} = -\log(5 \times 10^{-4}) + \log 4$$

$$= 3.30 + 0.602 = 3.902$$

$$\text{pH} = 14 - 3.902 = 10.09;$$

$$[\text{H}^+] = 8.1 \times 10^{-11} \approx 8 \times 10^{-11} \text{ M}$$

45. (1) : Reaction is balanced.

$$\text{Thus, } -4x = -4$$

$$\therefore x = 1$$

Thus, $\text{O}_2^{\cdot -}$ is O_2^- (Superoxide ion)

46. (9) : Given equation represents a straight line of

$$\text{slope} = -\frac{\Delta H^\circ}{2.303R} = \tan \theta = 0.5$$

where, negative sign shows that slope is decreasing.

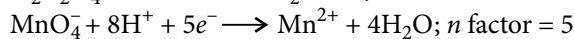
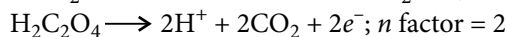
$$\text{intercept} = \log A = OP = 10$$

$$\log K = \log A - \frac{\Delta H^\circ}{2.303RT} = 10 - \frac{0.5}{298}$$

$$= 10 - 1.68 \times 10^{-3}$$

$$K = 9.96 \times 10^9$$

47. (1) : The reactions involved are :



No. of eq. of pure MnO_2 = No. of eq. of oxalic acid

= No. of eq. of KMnO_4 = No. of eq. of I_2

$$= \frac{0.0175}{127} \times 37.12 = 5.12 \times 10^{-3}$$

$$\text{Equivalent weight of MnO}_2 = \frac{87}{2} = 43.5$$

Weight of MnO_2 in pyrolusite

$$= 5.12 \times 10^{-3} \times 43.5 = 0.2227 \text{ g}$$

$$\text{Weight of pyrolusite} = \frac{100 \times 0.2227}{89.21} = 0.2496 \text{ g}$$

$$= 2.496 \times 10^{-1} \text{ g}$$

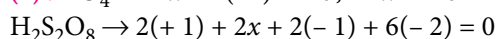
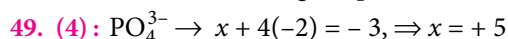
48. (2) : The two conditions when colour of indicator will be visible are derived by

$$\text{pH} = \text{p}K_a + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

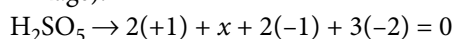
$$(i) \text{ pH} = 5 + \log 10 = 6$$

$$(ii) \text{ pH} = 5 + \log 0.1 = 4$$

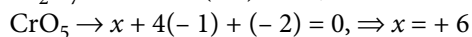
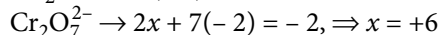
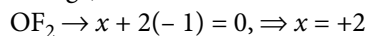
Thus, minimum change in $\text{pH} = 2$



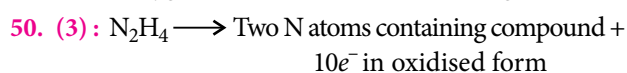
$\Rightarrow x = +6$ (Two oxygen atoms with peroxide linkage).



$\Rightarrow x = +6$ (Two oxygen atoms with peroxide linkage).



(Four oxygen atoms with peroxide linkage).



Oxidation number of N atom in N_2H_4 is -2 .

Thus, oxidation number of two N-atom in new compound

$$= -4 - (-10) = +6$$

$$\text{Thus, oxidation state of N} = \frac{6}{2} = +3$$



ACE

YOUR WAY CBSE XI



Series 2

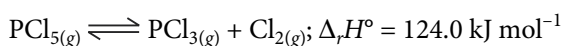
CHAPTERWISE UNIT TEST :

STATES OF MATTER | THERMODYNAMICS | EQUILIBRIUM | REDOX REACTIONS

GENERAL INSTRUCTIONS

- All questions are compulsory.
- Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- Q. no. 11 to 17 are also short answer questions and carry 3 marks each.
- Q. no. 18 is a value based question and carries 4 marks.
- Q. no. 19 and 20 are long answer questions and carry 5 marks each.
- Use log tables if necessary, use of calculators is not allowed.

- Air contains about 99% of N_2 and O_2 gases. Why do they not combine to form NO under the standard conditions? Standard Gibbs energy of formation of $NO_{(g)}$ is 86.7 kJ mol^{-1} .
 - Write an expression for Boyle temperature and critical temperature in terms of van der Waals' constants. Which one is larger for a particular gas?
 - Will the following reaction take place?
 $Ni_{(s)} + 2Ag^+_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$
 (Given, $E^\circ_{Ni^{2+}/Ni} = -0.25 \text{ V}$ and $E^\circ_{Ag^+/Ag} = +0.80 \text{ V}$)
 - What does the equilibrium constant $K < 1$ show?
 - The pK_a of acetic acid and pK_b of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution.
 - The solubility product of $Fe(OH)_3$ is 1×10^{-36} . What is the minimum concentration of OH^- ions required to precipitate $Fe(OH)_3$ from a 0.001 M solution of $FeCl_3$?
- OR**
- At 25°C , K_p for the reaction :
- $$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$
- has a value of 0.14 atm. Calculate the value of K_c in which the concentrations are measured in mol L^{-1} .
- The values of van der Waals' constant a for hydrogen and ammonia are $0.024 \text{ atm L}^2 \text{ mol}^{-2}$ and $4.17 \text{ atm L}^2 \text{ mol}^{-2}$ respectively. What conclusion do you draw from this data?
 - Under what conditions the following reactions can be spontaneous :
 (i) reaction with both ΔH and ΔS positive.
 (ii) reaction with both ΔH and ΔS negative.
 - Nitric acid is an oxidising agent and reacts with PbO but it does not react with PbO_2 . Explain why?
 - Two different gases 'A' and 'B' are filled in separate containers of equal capacity under the same conditions of temperature and pressure. On increasing the pressure slightly, the gas 'A' liquefies but gas 'B' does not liquefy even on applying high pressure until it is cooled. Explain this phenomenon.
 - At 473 K, equilibrium constant K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3} . If decomposition is depicted as :



- (i) What is the value of K_c for the reverse reaction at the same temperature?
- (ii) What would be the effect on K_c if (a) the pressure is increased (b) the temperature is increased?
12. The solubility product of $\text{Al}(\text{OH})_3$ is 2.7×10^{-11} . Calculate its solubility in g L^{-1} and also find out pH of this solution. (Atomic mass of Al = 27 u).
13. Balance the following equation by oxidation number method.
 $\text{K}_2\text{Cr}_2\text{O}_7 + \text{FeSO}_4 + \text{H}_2\text{SO}_4 \rightarrow$
 $\text{Cr}_2(\text{SO}_4)_3 + \text{Fe}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$
14. (i) Given that the enthalpy of formation of H_2O is -68 kcal/mol . Calculate the enthalpy of formation of OH^- ions.
- (ii) The standard enthalpies of formation of O_3 , CaO , NH_3 and HI are $+142.2 \text{ kJ}$, -634.9 kJ , -46 kJ and $+25.95 \text{ kJ}$ respectively. Arrange them in order of their increasing stability with respect to decomposition into their elements.
15. (i) Under what conditions, the electrode potential becomes standard?
- (ii) An iron rod is immersed in solution containing 1.0 M NiSO_4 and 1.0 M ZnSO_4 . Predict giving reasons, which of the following reactions is likely to proceed?
- (a) Fe reduces Zn^{2+} ions,
 (b) Iron reduces Ni^{2+} ions.
- Given : $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$, $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$ and $E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}$.
16. (i) The drain cleaner, Drainex contains small bits of aluminium which react with caustic soda to produce dihydrogen. What volume of dihydrogen at 20°C and one bar will be released when 0.15 g of aluminium reacts?
- (ii) What would have happened to the gas if the molecular collisions were not elastic?

OR

- (i) The relation between pressure exerted by an ideal gas (P_{ideal}) and observed pressure (P_{real}) is given by the equation

$$P_{\text{ideal}} = P_{\text{real}} + \frac{an^2}{V^2}$$

If pressure is taken in N m^{-2} , number of moles in mol and volume in m^3 , calculate the unit of 'a'.

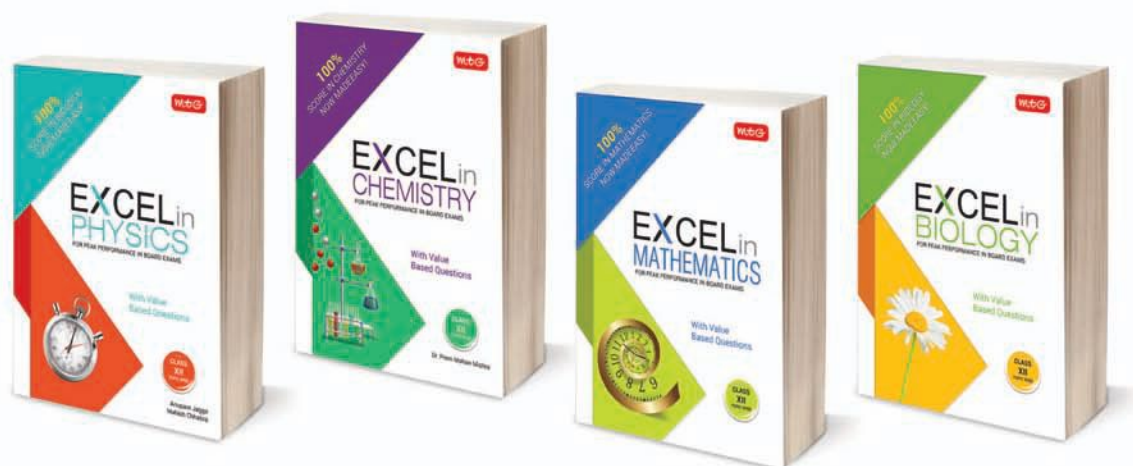
What will be the unit of 'a' when pressure is in atmosphere and volume in dm^3 ?

- (ii) Name two phenomena that can be explained on the basis of surface tension.
17. (i) What happens to the ionic product of water when HCl is added to it?
- (ii) Why sufficient amount of NH_4OH is added before $(\text{NH}_4)_2\text{CO}_3$ in group V qualitative analysis?
- (iii) Equilibrium constant, K_c for the reaction
 $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$
 at 500 K is 0.061 . At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L^{-1} of N_2 , 2.0 mol L^{-1} of H_2 and 0.5 mol L^{-1} of NH_3 . Is the reaction at equilibrium? If not, in which direction the reaction tend to proceed to reach equilibrium?
18. Puneet, a Class-XI student had severe toothache and he took some analgesic. His friend Rohan told him, that analgesics will give only temporary relief and took him to a dentist. Doctor prescribed some medicines and advised Puneet to brush his teeth after every meal and stop eating too much of sweets, chocolates and candies.
- (i) What values are displayed by Rohan?
- (ii) Why did the doctor asked Puneet to stop eating sweets?
- (iii) Give two examples from everyday life which show the effect of change in concentration on equilibrium.
19. The lattice enthalpy of an ionic compound is the enthalpy when one mole of an ionic compound present in its gaseous state, dissociates into its ions. It is impossible to determine it directly by experiment. Suggest and explain an indirect method to measure lattice enthalpy of $\text{NaCl}_{(s)}$.

OR

- (i) Why standard entropy of an elementary substance is not zero whereas standard enthalpy of formation is taken as zero?
- (ii) Propane (C_3H_8) is used for heating water for domestic supply. Assume that for 150 kg of hot water supply per day, water must be heated from 10°C to 65°C . How many moles and how much volume of propane in litres at STP would have to be used for heating this amount of water?

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($\Delta H_{\text{combustion}} \text{C}_3\text{H}_8 = -2050 \text{ kJ}$ and specific heat of water $= 4.184 \times 10^{-3} \text{ kJ g}^{-1}$)

(iii) Under what condition is the heat change equal to the internal energy change?

20. Which method can be used to find out strength of reductant/oxidant in a solution? Explain with an example.

OR

(i) Out of aluminium and silver vessel, which one will be more suitable to store 1 M HCl solution and why?

$$E^\circ_{\text{Al}^{3+}/\text{Al}} = -1.66 \text{ V}, E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$$

(ii) How will you compare acidic strength of oxyacids?

(iii) What are spectator ions?

SOLUTIONS

1. For the combination of N_2 and O_2 to form NO , the standard Gibbs energy of formation, is +ve ($+86.7 \text{ kJ mol}^{-1}$) therefore, this reaction is non-spontaneous under the standard conditions and hence, N_2 and O_2 do not combine.

2. Boyle temperature, $T_B = \frac{a}{bR}$

$$\text{Critical temperature, } T_C = \frac{8a}{27bR}$$

$$\therefore T_B > T_C$$

3. $E^\circ_{\text{Ni}^{2+}/\text{Ni}}$ has a negative value, thus it acts as a reducing agent and reduces Ag^+ ions to Ag atoms and therefore, the given reaction is feasible.

4. It shows that reaction is moving in backward direction. *i.e.*, it is farthest from completion.

5. Ammonium acetate is the salt of weak acid and weak base; pH can be calculated as :

$$\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_a - \text{p}K_b] = \frac{1}{2}[14 + 4.76 - 4.75] = 7.005$$

6. K_{sp} for $\text{Fe}(\text{OH})_3 = [\text{Fe}^{3+}][\text{OH}^-]^3$
Precipitation will occur when ionic product, $[\text{Fe}^{3+}][\text{OH}^-]^3$ becomes greater than K_{sp} .

$$[\text{Fe}^{3+}] = [\text{FeCl}_3] = 0.001 \text{ M}$$

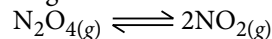
$$\therefore [\text{OH}^-]^3 = \frac{K_{sp}}{[\text{Fe}^{3+}]} = \left(\frac{1 \times 10^{-36}}{0.001} \right) = 1 \times 10^{-33}$$

$$\Rightarrow [\text{OH}^-] = (1 \times 10^{-33})^{1/3} = 1 \times 10^{-11} \text{ mol L}^{-1}$$

Thus, minimum concentration of OH^- required to start precipitation of $\text{Fe}(\text{OH})_3 = 1 \times 10^{-11} \text{ mol L}^{-1}$

OR

For the given reaction :



$$\Delta n_g = 2 - 1 = 1$$

$$K_p = K_c(RT)^{\Delta n_g}$$

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{0.14}{(0.082 \times 298)^1} = 5.73 \times 10^{-3} \text{ mol L}^{-1}$$

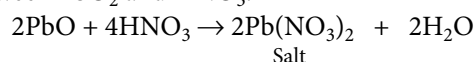
7. The value of van der Waals' constant a is a measure of attractive forces existing between the molecules of a given gas. These values suggest that van der Waals' forces of attraction are very weak in case of H_2 but are strong in case of NH_3 molecules. This is the reason that ammonia can be easily liquefied.

8. We know, $\Delta G = \Delta H - T\Delta S$,
the reaction will be spontaneous when ΔG is negative.

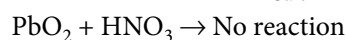
(i) If ΔH and ΔS both are positive then, ΔG will be negative when $T\Delta S > \Delta H$ which is possible at high temperature.

(ii) If ΔH and ΔS , both are negative then, ΔG will be negative when $\Delta H > T\Delta S$ which is possible at low temperature.

9. Nitric acid is an oxidising agent and reacts with PbO (basic oxide) to give a simple acid base reaction without any change in oxidation state of Pb . In PbO_2 , Pb is in +4 oxidation state and cannot be oxidised further hence, no reaction takes place between PbO_2 and HNO_3 .

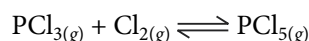


Salt



10. It shows that gas A attains its critical temperature with slight increase in pressure which means it is almost at its critical temperature. Gas B is at higher temperature than its critical temperature hence, it does not liquefy even after applying pressure until it is cooled.

11. (i) For the reverse reaction :

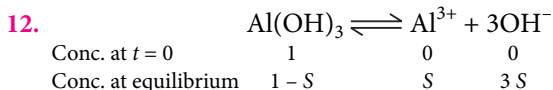


$$K'_c = \frac{1}{K_c} = \frac{1}{8.3 \times 10^{-3}} = 120.48$$

(ii) (a) The value of equilibrium constant is

constant for a particular reaction at a particular temperature hence, increase in pressure will have no effect.

- (b) As the reaction is endothermic, the increase in temperature will favour the forward reaction. More PCl_5 will dissociate to form PCl_3 and Cl_2 hence, K_c will increase.



$$K_{sp} = [\text{Al}^{3+}] [\text{OH}^-]^3 = (S) (3S)^3 = 27S^4$$

$$S^4 = \frac{K_{sp}}{27} = \frac{2.7 \times 10^{-11}}{27} = 1 \times 10^{-12}$$

$$S = 1 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{Molar mass of Al(OH)}_3 = 78 \text{ g}$$

$$\therefore \text{Solubility of Al(OH)}_3 \text{ in g L}^{-1} = 1 \times 10^{-3} \times 78$$

$$= 78 \times 10^{-3} = 7.8 \times 10^{-2} \text{ g L}^{-1}$$

pH of the solution :

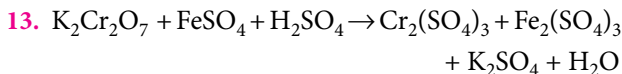
$$S = 1 \times 10^{-3} \text{ mol L}^{-1}$$

$$[\text{OH}^-] = 3S = 3 \times 1 \times 10^{-3} = 3 \times 10^{-3}$$

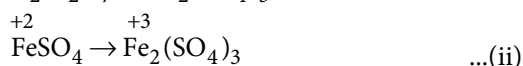
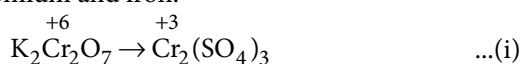
$$\text{pOH} = -\log[\text{OH}^-] = -\log(3 \times 10^{-3})$$

$$\text{pOH} = 3 - \log 3 = 3 - 0.4771 = 2.523$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.523 = 11.477$$



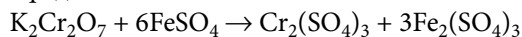
Change in oxidation number has occurred in chromium and iron.



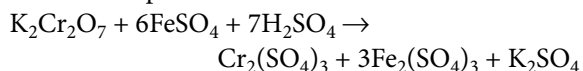
Decrease in oxidation number of Cr per molecule = 6

Increase in oxidation number of Fe per molecule = 1

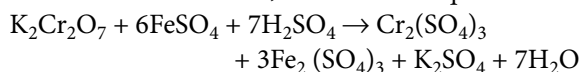
Hence, multiplying eq. (ii) by 6 and adding in eq. (i),



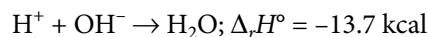
To balance sulphate ions and potassium ions, 7 molecules of H_2SO_4 and 1 molecule of K_2SO_4 are added to respective sides.



To balance hydrogen and oxygen, $7\text{H}_2\text{O}$ should be added on R.H.S. Hence, the balanced equation is



14. (i) For neutralisation reaction, we know that



$$\therefore \Delta_r H^\circ = \Delta_f H^\circ(\text{H}_2\text{O}) - [\Delta_f H^\circ(\text{H}^+) + \Delta_f H^\circ(\text{OH}^-)]$$

$$\text{i.e., } -13.7 = -68 - [0 + \Delta_f H^\circ(\text{OH}^-)]$$

$$[\because \Delta_f H^\circ(\text{H}^+) = 0]$$

$$\text{or } \Delta_f H^\circ(\text{OH}^-) = -68 + 13.7$$

$$= -54.3 \text{ kcal mol}^{-1}$$

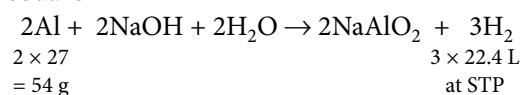
- (ii) In general, those compounds which are formed by absorption of heat are less stable than those formed with release of heat because lesser the energy, more stable is the system (compound). Therefore, increasing stability of the given compounds is in the order :



15. (i) The electrode potential is generally measured under standard conditions, i.e., 1 molar concentration of the ions with respect to which the electrode is reversible at 298 K and 1 atmospheric pressure is called standard electrode potential and is denoted by E° .

- (ii) (a) Since, E° of Zn is more negative than that of Fe, therefore, Zn will be oxidised to Zn^{2+} ions while Fe^{2+} ions will be reduced to Fe. Hence, Fe will not reduce Zn^{2+} ions.
- (b) Since, E° of Fe is more negative than that of Ni therefore, Fe will be oxidised to Fe^{2+} ions while Ni^{2+} ions will be reduced to Ni. Thus, Fe reduces Ni^{2+} ions.

16. (i) The reaction between aluminium and caustic soda is



54 g of Al produces H_2 at S.T.P. = $3 \times 22.4 \text{ L}$

0.15 g of Al will produce H_2 at S.T.P.

$$= \frac{3 \times 22.4}{54} \times 0.15 = 0.186 \text{ L}$$

At STP

$$P_1 = 1 \text{ atm}$$

$$V_1 = 0.186 \text{ L}$$

$$T_1 = 273 \text{ K}$$

Given conditions

$$P_2 = 1 \text{ bar} = 0.987 \text{ atm}$$

$$V_2 = ?$$

$$T_2 = 273 + 20 = 293 \text{ K}$$

Applying ideal gas equation, $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\frac{1 \times 0.186}{273} = \frac{0.987 \times V_2}{293}$$

$$V_2 = \frac{293}{0.987} \times \frac{1 \times 0.186}{273} = 0.2023 \text{ L} = 202.3 \text{ mL}$$

- (ii) On every collision, there would have been loss

of energy. As a result, the molecules would have slowed down and ultimately settle down in the vessel. Moreover, the pressure would have gradually reduced to zero.

OR

$$(ii) P_{ideal} = P_{real} + \frac{an^2}{V^2}$$

Writing units,

$$Nm^{-2} = Nm^{-2} + \frac{a \text{ mol}^2}{(m^3)^2}$$

$$\text{or } Nm^{-2} = \frac{a \text{ mol}^2}{m^6}$$

$$\text{or } a = \frac{Nm^{-2} m^6}{\text{mol}^2}$$

$$\Rightarrow a = Nm^4 \text{ mol}^{-2}$$

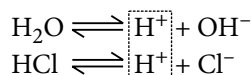
When pressure is in atm and volume in dm^3 then,

$$\text{atm} = \frac{a(\text{mol})^2}{(\text{dm}^3)^2}$$

$$a = \frac{\text{atm dm}^6}{(\text{mol})^2} = \text{atm dm}^6 \text{ mol}^{-2}$$

- (ii) (a) Spherical shape of liquid drops.
(b) Rise or fall of liquid in a capillary.

17. (i) There is no effect of addition of HCl to the ionic product of water due to common ion effect, i.e., $[H^+]$ concentration increases while $[OH^-]$ concentration decreases accordingly so that the product $[H^+][OH^-]$ remains the same.



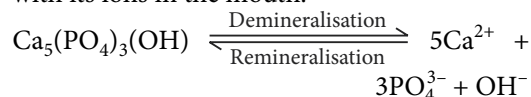
- (ii) Ammonium carbonate usually contains ammonium bicarbonate with it. As a result the cations of group V will form not only insoluble carbonates but soluble bicarbonates as well and the precipitation will not be complete. Thus, ammonium hydroxide is added to convert ammonium bicarbonate into ammonium carbonate.

$$(iii) \text{ Here, } Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.5)^2}{(3.0)(2.0)^3} = 0.0104$$

As $Q_c \neq K_c$, the reaction is not at equilibrium and $Q_c < K_c$ therefore, the reaction will proceed in the forward direction.

18. (i) Rohan showed the values of awareness by suggesting that disease should be cured by eliminating its cause and not by controlling only its symptoms by analgesics and concern towards his friend's well being.

- (ii) Sweet substances cause tooth decay. An enamel of insoluble substance called hydroxyapatite, $Ca_5(PO_4)_3(OH)$, is present in the form of a thin coating on our teeth. It exists in equilibrium with its ions in the mouth.



When sugar substances are taken, these are absorbed on teeth and if not removed these get fermented producing H^+ ions. The H^+ ions disturb the above equilibrium by combining with OH^- ions to form water and with PO_4^{3-} ions to form HPO_4^{2-} ions. Thus, the sweet substances shift the above equilibrium to the right-hand side, thereby causing tooth decay.

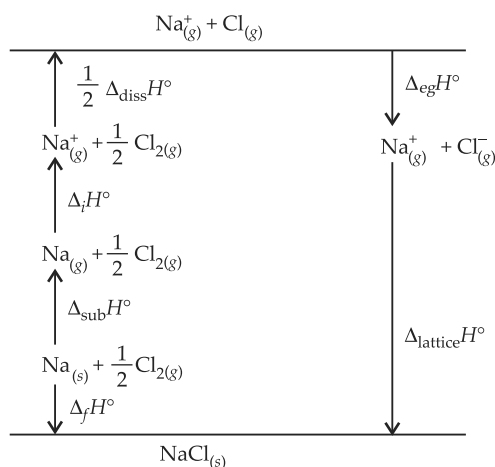
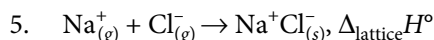
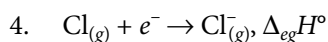
- (iii) (a) Removal of carbon dioxide from the tissues by blood : The equilibrium is,
 $CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} \rightleftharpoons H_{(aq)}^+ + HCO_{(aq)}^{3-}$

Carbon dioxide dissolves in blood on account of high partial pressure of carbon dioxide in tissues. The same blood, when comes to lungs, releases the dissolved carbon dioxide as the partial pressure of carbon dioxide is low here.

- (b) Faster drying of clothes when there is a breeze : When there is a breeze, the water vapours of the nearby air are removed. In order to re-establish the equilibrium, the wet cloth loses more water in the vapour state to saturate the surrounding air and hence gets dried.

19. Lattice enthalpy can be measured with the help of Born-Haber cycle in which an enthalpy diagram is constructed to calculate lattice enthalpy. For calculating the lattice enthalpy of NaCl following steps are taken into consideration.

1. $Na_{(s)} \rightarrow Na_{(g)}, \Delta_{\text{sub}}H^\circ$
2. $Na_{(g)} \rightarrow Na_{(g)}^+ + e^-, \Delta_iH^\circ$
3. $\frac{1}{2} Cl_{2(g)} \rightarrow Cl_{(g)}, \frac{1}{2} \Delta_{\text{diss}}H^\circ$



Applying Hess's law,

$$\Delta_f H^\circ = \Delta_{\text{sub}} H^\circ + \Delta_i H^\circ + \Delta_{eg} H^\circ + \frac{1}{2} \Delta_{\text{diss}} H^\circ + \Delta_{\text{lattice}} H^\circ$$

OR

- (i) A substance has a perfectly ordered arrangement of its constituent particles only at absolute zero. Hence, entropy is zero only at absolute zero. Enthalpy of formation is the heat change involved in the formation of one mole of the substance from its elements. An element formed from itself means no heat change, *i.e.*, $\Delta_f H^\circ = 0$.

- (ii) Heat energy required for heating water

$$\begin{aligned} q &= m \times s \times \Delta T \\ &= 150 \times 10^3 \times 4.184 \times 10^{-3} (65 - 10) \\ &= 34518 \text{ kJ} \end{aligned}$$

$$\Delta H_{\text{combustion}} \text{C}_3\text{H}_8 = -2050 \text{ kJ}$$

i.e., 2050 kJ heat is obtained by burning 1 mole of propane

\therefore 34518 kJ heat will be obtained from

$$= \frac{1 \times 34518}{2050} \text{ moles} = 16.84 \text{ moles of propane}$$

Volume of 16.84 moles of propane at STP

$$\begin{aligned} &= 16.84 \times 22.4 \text{ L} \\ &= 372.2 \text{ L} \end{aligned}$$

- (iii) Heat change is equal to the internal energy change when volume is kept constant.

$$\Delta H = \Delta U + P\Delta V$$

when $\Delta V = 0$

$$\Delta H = \Delta U$$

20. The method used is by connecting the redox couple of the given species with standard hydrogen electrode. Then the value of electrode potential will determine the strength of oxidant/reductant. If the value comes out to be positive then the species acts as the oxidant and if the value is negative then the species acts as the reductant. So, higher is the value of electrode potential, higher is the strength of species to act as oxidant and vice versa.

For example, when Zn^{2+}/Zn electrode is connected with SHE then the EMF of the cell is 0.76 V. Here, Zn^{2+}/Zn acts as anode and SHE as cathode.

$$\begin{aligned} \therefore E_{\text{cell}}^\circ &= 0.76 \text{ V} = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \\ 0.76 &= 0 - E_{\text{anode}}^\circ \Rightarrow E_{\text{anode}}^\circ = -0.76 \text{ V} \end{aligned}$$

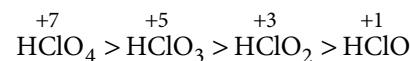
OR

- (i) Since, reduction potential of silver is more than that of hydrogen ($E_{\text{H}^+/\text{H}_2}^\circ$, Pt = 0), silver vessel will be suitable to store 1 M HCl. On the other hand, $E_{\text{Al}^{3+}/\text{Al}}^\circ$ is less than that of hydrogen ($E_{\text{H}^+/\text{H}_2}^\circ$, Pt), so that hydrogen will be liberated if stored in aluminium vessel.

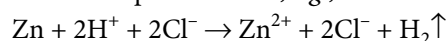
- (ii) For any series of oxyacids, the one in which the atom bonded to oxygen is in the highest oxidation state is the strongest acid.

e.g., HNO_3 is stronger than HNO_2 ; H_2SO_4 is stronger than H_2SO_3 .

The strength of oxyacids of chlorine decreases in the order.



- (iii) Species that are present in the solution but do not take part in the reaction and are also omitted while writing the net ionic reaction are called spectator ions, *e.g.*,



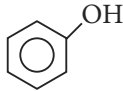
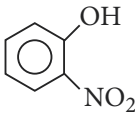
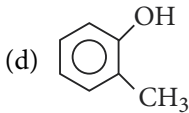
In this reaction Cl^- ions are omitted and are called spectator ions as they appear on the reactants as well as the products side.



BIHAR CECE

SECOND STAGE

SOLVED PAPER 2015

- In which of the following pairs, each member produces the same gas when reacts with water?
(a) K, KO₂ (b) Na, Na₂O₂
(c) Ca, CaH₂ (d) Ba, BaO₂
- The volume strength of 1.5 N H₂O₂ solution is
(a) 4.8 litres (b) 5.2 litres
(c) 8.4 litres (d) 8.8 litres.
- In which of the following, the ratio of the sizes of cation to anion is smallest?
(a) NaCl (b) KCl
(c) MgCl₂ (d) CaF₂
- A solid 'x' on heating gives CO₂ and a residue. The residue with H₂O form 'y'. On passing an excess of CO₂ through 'y' in H₂O, a clear solution of 'z' is obtained. On boiling 'z', 'x' is reformed. 'x' is :
(a) Ca(HCO₃)₂ (b) CaCO₃
(c) Na₂CO₃ (d) K₂CO₃
- Which is the most basic oxide?
(a) ZnO (b) MgO
(c) Al₂O₃ (d) N₂O₅
- Al₂O₃ becomes anhydrous AlCl₃ upon heating
(a) with NaCl (b) with dry Cl₂ + C
(c) with Cl₂ (d) with dry HCl gas.
- Which of the following is not formed?
(a) NCl₅ (b) AsF₅
(c) SbCl₅ (d) PF₅
- The product of $\text{NH}_2 - \text{NH}_2 + \text{H}_2\text{O}_2 \xrightarrow{\text{Cu}^{2+}}$ is
(a) O₂ (b) H₂
(c) NH₃ (d) N₂
- The colour of liquid O₂ is
(a) pale yellow (b) pale blue
(c) green (d) red.
- The basicity of H₃PO₃ is
(a) 1 (b) 2
(c) 3 (d) none of these.
- CrO₃ dissolves in aqueous NaOH to give
(a) Cr₂O₇²⁻ (b) CrO₄²⁻
(c) Cr(OH)₃ (d) Cr(OH)₂
- The following ion in its aqueous solution is colourless :
(At. no. : Sc = 21, Fe = 26, Ti = 22, Mn = 25)
(a) Sc³⁺ (b) Fe²⁺
(c) Ti³⁺ (d) Mn²⁺
- The oxidation number of Ni in [Ni(C₂O₄)₃]⁴⁻ is
(a) 3 (b) 4
(c) 2 (d) 6
- Which of the following is an optically active compound?
(a) 1-butanol (b) 1-propanol
(c) 2-chlorobutane (d) 4-hydroxy heptane
- In sodium fusion test of organic compounds, N is converted to
(a) NaNH₂ (b) NaCN
(c) NaNO₂ (d) NaNO₃
- Which one of the following is called inorganic graphite?
(a) B (b) B₄C
(c) B₂H₆ (d) BN
- Glass + HF → ?
(a) SiF₄ (b) H₂SiF₆
(c) H₂SiO₃ (d) Na₃AlF₆
- How many chiral C are there in β-D-(+)-glucose?
(a) 5 (b) 6
(c) 3 (d) 4
- Which is the strongest acid?
(a) Cl-CH₂-CH₂-OH (b) 
(c) 
(d) 

Contributed by : Paradise Institute, Patna

20. This compound forms a sodium salt upon reacting with NaNH_2
 (a) C_2H_2 (b) CH_3NH_2
 (c) C_6H_6 (d) C_2H_6
21. What is the electrophile when $\text{RCl} + \text{AlCl}_3$ are used in Friedel Craft reaction?
 (a) Cl^+ (b) AlCl_4^-
 (c) R^+ (d) AlCl_2^+
22. Nylon-6 is made from
 (a) isoprene (b) adipic acid
 (c) caprolactam (d) styrene.
23. Which polymer has different type of bond between monomers from the other three?
 (a) Cellulose (b) Wool
 (c) Silk (d) Nylon
24. In Buna-S, S stands for
 (a) sulphur (b) soft
 (c) styrene (d) sodium.
25. Which one is incorrect name?
 (a) Propyne (b) But-2-yne
 (c) Pent-3-yne (d) But-1-yne
26. Lewisite, a war gas, is made by reacting $\text{CH}\equiv\text{CH}$ with
 (a) HCN (b) HCl
 (c) AsCl_3 (d) O_3
27. The product of $\text{CH}\equiv\text{CH} \xrightarrow[\text{Hg}^{2+}]{\text{CH}_3\text{COOH}}$ is
 (a) $\text{CH}_2=\text{CHCl}$ (b) $\text{CH}_3\text{CH}(\text{OOCCH}_3)_2$
 (c) CH_3CHO (d) $\text{CH}_3\text{CH}_2\text{CHO}$
28. $(\text{C}_2\text{H}_5)_4\text{Pb}$ is an example of
 (a) negative catalyst (b) positive catalyst
 (c) solvent (d) fuel
29. Which metal is used as a part of catalyst in Fischer-Tropsch method?
 (a) Mn (b) Co
 (c) Fe (d) Pt
30. The octane number of this alkane is 100 :
 (a) 2, 2, 4-Trimethylpentane
 (b) Hexane
 (c) Heptane
 (d) Butane
31. Identify organometallic compound(s).
 (a) CH_3ONa (b) $\text{C}_2\text{H}_5\text{SNa}$
 (c) CH_3MgI (d) All of these.
32. Which one is called Westrosol?
 (a) CCl_4 (b) $\text{CCl}_2=\text{CHCl}$
 (c) CHCl_3 (d) $\text{CHCl}_2\text{CHCl}_2$
33. $\text{CH}_3\text{CH}_2\text{OH} + \text{HI} \xrightarrow[\text{H}_2\text{O}]{+ \text{Sn}} \text{CH}_3\text{CH}_2\text{I} \xrightarrow{+ \text{X}} \text{Y}$
 $\xrightarrow{+ \text{HCl}} \text{CH}_3\text{CH}_2\text{OH}$, X is
 (a) NaHS (b) NaNO_2
 (c) AgNO_2 (d) AgNO_3
34. $\text{X} + \text{Br}_2 \longrightarrow \text{CH}_3\text{CH}_2\text{Br} + \text{a gas} + \text{a salt}$. X is
 (a) $\text{CH}_3\text{CH}_2\text{OH}$ (b) CH_3COONa
 (c) $\text{CH}_3\text{CH}_2\text{SH}$ (d) $\text{CH}_3\text{CH}_2\text{COOAg}$
35. Which is hygroscopic, sweet in taste and non-poisonous?
 (a) CH_3OH
 (b) $\text{CH}_2\text{OH}\cdot\text{CHOH}\cdot\text{CH}_2\text{OH}$
 (c) CH_3OCH_3
 (d) $\text{CH}_3\text{CH}_2\text{OH}$
36. Which is used as a solvent during reactions with Grignard reagent?
 (a) $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ (b) $\text{C}_2\text{H}_5\text{OH}$
 (c) $\text{C}_2\text{H}_5\text{NH}_2$ (d) CCl_4
37. This is added to ether to test its purity :
 (a) $\text{C}_2\text{H}_5\text{ONa}$ (b) KI
 (c) KCl (d) $\begin{array}{c} \text{CH}_3\text{CO} \diagup \text{O} \\ \text{CH}_3\text{CO} \diagdown \end{array}$
38. This is oxidised to prepare methyl ethyl ketone :
 (a) 2-propanol (b) 1-butanol
 (c) 2-butanol (d) *t*-butyl alcohol
39. This does not convert a ketone to an alcohol :
 (a) $\text{Zn/Hg} + \text{HCl}$ (b) Ni
 (c) LiAlH_4 (d) $\text{Na/Hg} + \text{H}_2\text{O}$
40. The number of isomeric aldehydes for $\text{C}_5\text{H}_{10}\text{O}$ is
 (a) 2 (b) 3
 (c) 5 (d) 4
41. Which is a mixed ketone?
 (a) Propan-2-one (b) Butan-2-one
 (c) Pentan-3-one (d) None of these.
42. This does not react with Fehling's solution :
 (a) CH_3CHO (b) $(\text{CH}_3)_2\text{CO}$
 (c) HCHO (d) HCOOH
43. This does not undergo aldol condensation :
 (a) HCHO (b) CH_3CHO
 (c) CH_3COCH_3 (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$

44. Acrolein is
 (a) ketone (b) aldehyde
 (c) polymer (d) protein.
45. $\text{FeSO}_4 + \text{H}_2\text{O}_2$ is called
 (a) Fehling's solution (b) Benedict's solution
 (c) Schiff's reagent (d) Fenton's reagent.
46. $\text{CH}_3\text{CN} \xrightarrow{\text{H}_2\text{O}_2 + \text{OH}^-} \text{X}$
 $\text{CH}_3\text{CN} \xrightarrow{\text{HCl}} \text{Y}$
 The compounds X and Y are respectively
 (a) $\text{CH}_3\text{CH}_2\text{NH}_2$, CH_3COCl
 (b) CH_3CONH_2 , $\text{CH}_3\text{CH}_2\text{Cl}$
 (c) CH_3COOH , CH_3CONH_2
 (d) CH_3CONH_2 , CH_3COOH
47. Dry distillation of $(\text{CH}_3\text{COO})_2\text{Ca}$ produces
 (a) CH_3COOH (b) CH_3CHO
 (c) $(\text{CH}_3)_2\text{CO}$ (d) $\text{CH}_3\text{COOCH}_3$
48. Electrolysis of a concentrated aqueous solution of a compound gave C_2H_6 on anode. The compound is
 (a) CH_3COOK (b) $\text{CH}_3\text{CH}_2\text{COOK}$
 (c) $\text{CH}_3\text{COOC}_2\text{H}_5$ (d) CH_3OCH_3
49. The product of $\text{CO} + \text{NaOH} \xrightarrow[10 \text{ atm}]{210^\circ\text{C}}$ is
 (a) CO_2 (b) CH_3COONa
 (c) HCOONa (d) CH_4
50. The compound insoluble in acetic acid is
 (a) CaO (b) CaCO_3
 (c) $\begin{array}{c} \text{COO} \\ | \\ \text{COO} \end{array} \text{Ca}$ (d) $\text{Ca}(\text{OH})_2$
51. Alkaline hydrolysis of an ester is called
 (a) neutralization (b) esterification
 (c) polymerization (d) saponification.
52. What is biuret?
 (a) $\text{CH}_3\text{CONH}_2\text{CH}_3$ (b) $\text{NH}_2\text{CONHCONH}_2$
 (c) NH_2CONH_2 (d) NH_2OH
53. What is grape-sugar?
 (a) Strach (b) Glucose
 (c) Fructose (d) Sucrose
54. How many stereoisomers does α -D-glucose has?
 (a) 10 (b) 13 (c) 15 (d) 6
55. What is the bond between monosaccharides in starch?
 (a) Glycosidic (b) Peptide
 (c) Phosphodiester (d) Ester
56. Glucose reacts with
 (a) Schiff's reagent (b) Phenyl hydrazine
 (c) NaHSO_3 (d) $\text{Br}_2 + \text{H}_2\text{O}$
57. Which one is an aldoketose?
 (a) Fructose (b) Glucose
 (c) Maltose (d) Starch
58. The formula of vitamin C is
 (a) $\text{C}_9\text{H}_{17}\text{O}_5\text{N}$ (b) $\text{C}_6\text{H}_8\text{O}_6$
 (c) $\text{C}_6\text{H}_5\text{NO}_2$ (d) $\text{C}_{19}\text{H}_{19}\text{N}_7\text{O}_6$
59. This is not water soluble vitamin
 (a) D (b) C
 (c) B_1 (d) Folic acid
60. The deficiency of this vitamin makes it difficult to see in dim light
 (a) A (b) B
 (c) C (d) D
61. This vitamin is less available to vegetarians
 (a) A (b) B_{12}
 (c) B_2 (d) C
62. In the benzene sulphonation, the active species is
 (a) HSO_4^- (b) SO_3 (c) SO_2 (d) SO_4^{2-}
63. Benzene has
 (a) 3 delocalized electrons
 (b) 4 delocalized electrons
 (c) 6 delocalized electrons
 (d) 12 delocalized electrons.
64. This is a meta directing group in monosubstituted benzene during substitution reactions :
 (a) $-\text{C} \equiv \text{N}$ (b) $-\text{NH}_2$
 (c) $-\text{OH}$ (d) $-\text{O}^-$
65. An organic compound contains C = 40%, H = 6.66% and rest is oxygen. The empirical formula of the compound is
 (a) CH_2O (b) CHO
 (c) $\text{C}_2\text{H}_4\text{O}_2$ (d) CH_3OH
66. Paper chromatography has following mobile and stationary phases respectively
 (a) liquid, solid (b) solid, liquid
 (c) gas, liquid (d) liquid, liquid
67. In Lassaigne's test, the following reagent is used for testing the presence of both N and S
 (a) AgNO_3 (b) FeCl_3
 (c) Na_2S (d) $\begin{array}{c} \text{CH}_3\text{COO} \\ | \\ \text{CH}_3\text{COO} \end{array} \text{Pb}$

68. For a second order reaction $k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$ if the concentration of two reactants A and B are
 (a) $[A] = [B]$ (b) $[A] > [B]$
 (c) $[A] < [B]$ (d) In all cases.
69. 100 mL H_2O and 50 mL ether were mixed with succinic acid. At equilibrium, ether phase had 0.127 g and H_2O phase had 1.843 g succinic acid. The distribution constant of succinic acid between water-ether
 (a) 7.25 (b) 14.50
 (c) 3.62 (d) 10
70. The van't Hoff factor of benzoic acid solution in benzene is 0.5. In this solution, benzoic acid
 (a) dissociates
 (b) forms dimer
 (c) remains unchanged
 (d) forms tetramer.
71. $pH + pOH$ is equal to
 (a) 0 (b) 7 (c) 14 (d) 10
72. In DNA, the complementary base pairs are
 (a) A and T, G and C (b) G and A, T and C
 (c) A and T, G and U (d) U and A, C and G
73. At what temperature a reaction will be at equilibrium at 1 atm if ΔH and ΔS are 30.58 kJ and 66.1 J K^{-1} respectively? These values do not change with temperature in any significant fashion.
 (a) 420.2 K (b) 462.6 K
 (c) 429 K (d) 642 K
74. 10 g hydrogen is reacted with 64 g oxygen. The amount of water formed will be (in moles)
 (a) 3 (b) 4 (c) 1 (d) 2
75. In Freundlich adsorption isotherm, the value of $\frac{1}{n}$ is between
 (a) 0 and 1 (b) 0 and 0.1
 (c) 2 and 4 (d) 1 and 10
76. Dettol is a mixture of
 (a) terpineol and bithional
 (b) chloroxyleneol and bithional
 (c) chloroxyleneol and terpineol
 (d) phenol and iodine.
77. What is not produced within human body?
 (a) Vitamin (b) Hormone
 (c) Enzyme (d) DNA
78. Which one is an anti-histamine?
 (a) Chloramphenicol (b) Diphenylhydramine
 (c) Norothindrone (d) Omeprazole
79. Waxes are
 (a) hydrocarbons (b) esters
 (c) amines (d) fatty acids.
80. Which one is a set of isoelectronic species?
 (a) N_2 , CO_2 , CN^- (b) N, H_2S , CO
 (c) N_2 , CO, CN^- (d) Ca, Mg, Cl
81. The solution of this compound will show maximum ionic conductivity:
 (a) $K_4[Fe(CN)_6]$ (b) $[Co(NH_3)_6]Cl_3$
 (c) $[Cu(NH_3)_4]Cl_2$ (d) $[Ni(CO)_4]$
82. Which one is paramagnetic?
 [At. no. Cr = 24, Fe = 26]
 (a) $[Cr(CO)_6]$ (b) $[Fe(CO)_5]$
 (c) $[Fe(CN)_6]^{4-}$ (d) $[Cr(NH_3)_6]^{3+}$
83. Which is paramagnetic?
 (a) Cl_2O (b) ClO_2
 (c) Cl_2O_7 (d) Cl_2O_6
84. If saturated solution of $Ba(OH)_2$ has pH of 12, its K_{sp} is
 (a) $4 \times 10^{-6} M^3$ (b) $4 \times 10^{-7} M^3$
 (c) $5 \times 10^{-6} M^3$ (d) $5 \times 10^{-7} M^3$
85. Pure water can be obtained from sea water by
 (a) centrifugation (b) plasmolysis
 (c) reverse osmosis (d) sedimentation
86. Standard electrode potential values :
 Fe^{2+}/Fe , $E^\circ = -0.44$, Fe^{3+}/Fe^{2+} , $E^\circ = 0.77$
 If Fe^{2+} , Fe^{3+} and Fe blocks are kept together, it will lead to
 (a) increase in Fe^{3+} (b) decrease in Fe^{3+}
 (c) $\frac{Fe^{2+}}{Fe^{3+}}$ remains unchanged
 (d) Fe^{2+} decreases.
87. Which will have highest number of isomers?
 (a) $[Co(NH_3)_4Cl_2]$ (b) $[Ni(C_2O_4)(en)_2]^{2-}$
 (c) $[Ni(en)(NH_3)_4]^{2+}$ (d) $[Cr(SCN)_2(NH_3)_4]^+$
88. The rate $\frac{d[B]}{dt}$ for reaction $3A \longrightarrow 2B$ is equal to
 (a) $-\frac{3}{2} \frac{d[A]}{dt}$ (b) $-\frac{2}{3} \frac{d[A]}{dt}$
 (c) $-\frac{1}{3} \frac{d[A]}{dt}$ (d) $+2 \frac{d[A]}{dt}$

89. Which one has $p_\pi - d_\pi$ bond?
 (a) NO_3^- (b) SO_3^{2-} (c) BO_3^{3-} (d) CO_3^{2-}
90. Serpeck's process is used for bauxite which has following main impurity
 (a) SiO_2 (b) Fe_2O_3 (c) Fe_3O_4 (d) CaO
91. An ideal solution is formed when its components
 (a) upon mixing show no change in volume
 (b) upon mixing show no change in enthalpy
 (c) upon mixing show neither change in volume nor enthalpy
 (d) show high solubility.
92. Which one of the following have same van't Hoff factor as that of $\text{K}_4[\text{Fe}(\text{CN})_6]$?
 (a) $\text{Al}_2(\text{SO}_4)_3$ (b) NaCl
 (c) $\text{Al}(\text{NO}_3)_3$ (d) Na_2SO_4
93. How many kg of O_2 will be required for complete combustion of 2.8 kg of ethylene?
 (a) 2.8 (b) 6.4 (c) 9.6 (d) 96
94. The number of moles of KMnO_4 needed to react with 1 mole of SO_3^{2-} in acidic solution is
 (a) $\frac{4}{5}$ (b) $\frac{2}{5}$ (c) 1 (d) $\frac{3}{5}$
95. Acetylene has following bonds between the carbon atoms
 (a) $1\sigma, 2\pi$ (b) 3σ
 (c) 3π (d) $2\sigma, 1\pi$
96. At CMC, surfactant molecules
 (a) hydrolyse (b) dissociate
 (c) associate (d) dissolve completely.
97. For the reaction $\text{CO}_{(g)} + \text{Cl}_{2(g)} \rightleftharpoons \text{COCl}_{2(g)}$, K_p/K_c is equal to
 (a) \sqrt{RT} (b) RT (c) $\frac{1}{RT}$ (d) 1.0
98. The conjugate base of OH^- is
 (a) O^{2-} (b) O^- (c) H_2O (d) O_2
99. The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed
 (a) $10^{-4} \text{ M Ca}^{2+} + 10^{-4} \text{ M F}^-$
 (b) $10^{-2} \text{ M Ca}^{2+} + 10^{-3} \text{ M F}^-$
 (c) $10^{-5} \text{ M Ca}^{2+} + 10^{-3} \text{ M F}^-$
 (d) $10^{-3} \text{ M Ca}^{2+} + 10^{-5} \text{ M F}^-$
100. Washing soda is
 (a) $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ (b) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
 (c) $\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ (d) Na_2CO_3

ANSWER

KEYS

- | | | | | |
|-----------|------------|---------|---------|----------|
| 1. (c) | 2. (c) | 3. (c) | 4. (b) | 5. (b) |
| 6. (b) | 7. (a) | 8. (d) | 9. (b) | 10. (b) |
| 11. (b) | 12. (a) | 13. (c) | 14. (c) | 15. (b) |
| 16. (d) | 17. (b) | 18. (a) | 19. (c) | 20. (a) |
| 21. (c) | 22. (c) | 23. (a) | 24. (c) | 25. (c) |
| 26. (c) | 27. (b) | 28. (a) | 29. (b) | 30. (a) |
| 31. (c) | 32. (b) | 33. (d) | 34. (d) | 35. (b) |
| 36. (a) | 37. (b) | 38. (c) | 39. (a) | 40. (d) |
| 41. (b) | 42. (b) | 43. (a) | 44. (b) | 45. (d) |
| 46. (d) | 47. (c) | 48. (a) | 49. (c) | 50. (c) |
| 51. (d) | 52. (b) | 53. (b) | 54. (c) | 55. (a) |
| 56. (b,d) | 57. (None) | 58. (b) | 59. (a) | 60. (a) |
| 61. (b) | 62. (b) | 63. (c) | 64. (a) | 65. (a) |
| 66. (d) | 67. (b) | 68. (a) | 69. (a) | 70. (b) |
| 71. (c) | 72. (a) | 73. (b) | 74. (b) | 75. (a) |
| 76. (c) | 77. (a) | 78. (b) | 79. (b) | 80. (c) |
| 81. (a) | 82. (d) | 83. (b) | 84. (d) | 85. (c) |
| 86. (b) | 87. (d) | 88. (b) | 89. (b) | 90. (a) |
| 91. (c) | 92. (a) | 93. (c) | 94. (b) | 95. (a) |
| 96. (c) | 97. (c) | 98. (a) | 99. (b) | 100. (b) |

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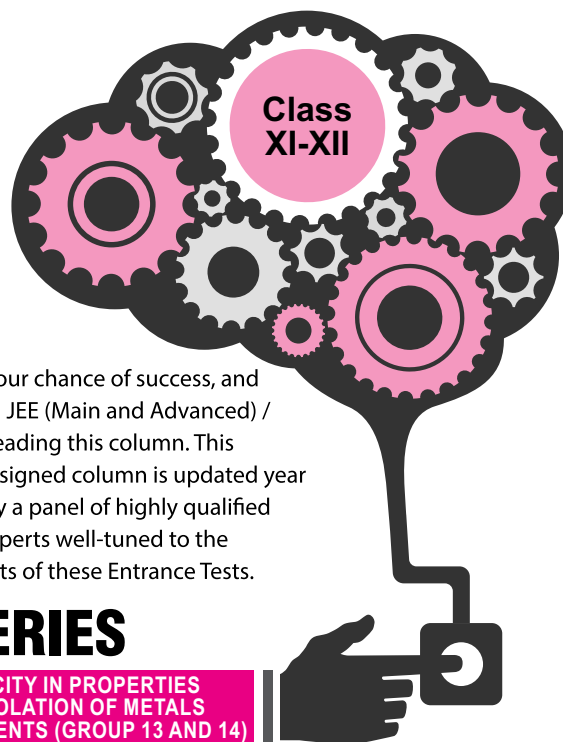
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JEE

ACCELERATED LEARNING SERIES

Unit 4

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES
GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF METALS
HYDROGEN | s-BLOCK ELEMENTS | p-BLOCK ELEMENTS (GROUP 13 AND 14)



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CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

- Modern Periodic Law
- Present Form of the Periodic Table
- Periodic Trends

TIPS TO REMEMBER

Modern Periodic Law

- The physical and chemical properties of elements are periodic functions of their atomic numbers.
- If the elements are arranged in increasing order of their atomic numbers, there is repetition of properties after 2, 8, 8, 18, 18 and 32 elements due

to repetition of similar electronic configuration of the outermost orbit.

Present Form of the Periodic Table

- The present form of periodic table consists of 18 vertical columns and 7 horizontal rows in which elements are arranged in such a way that elements with similar electronic configurations are placed in the same vertical column. Further, 14 elements of sixth period called the *lanthanoids* and 14 elements of seventh period called the *actinoids* are placed in separate panels at the bottom.

The diagram illustrates the modern periodic table with the following details:

- Groups:** 1 to 18.
- Periods:** 1 to 7.
- Blocks:**
 - s-block:** Groups 1 and 2, labeled (ns^1-2) .
 - d-block:** Groups 3 to 10, labeled $[(n-1)d^1-10 ns^1-2]$.
 - p-block:** Groups 13 to 18, labeled $(ns^2 np^1-6)$.
 - f-block:** Lanthanoids and Actinoids, labeled $(n-2)f^1-14 (n-1)d^0-1 ns^2$.
- Element Classification:**
 - Reactive metals: Groups 1 and 2.
 - Transition metals: Groups 3 to 10.
 - Inner-transition metals: Lanthanoids and Actinoids.
 - Poor metals: Groups 11 and 12.
 - Metalloids: Groups 13 to 16.
 - Non-metals: Groups 17 and 18.
- Series:** 3d-series, 4d-series, 5d-series, 6d-series, 4f-series, 5f-series.
- Other Labels:** Alkali metals, Alkaline earth metals, Coinage metals, Pnictogens, Chalcogens, Halogens, Noble gases.

Modern periodic table

Periodic Trends

❑ **Atomic radius** : It refers to the distance between the centre of nucleus of an atom to its outermost shell of electrons.

○ Absolute value of atomic radius cannot be determined because of the following reasons.

- The exact position of the valence shell is uncertain according to Heisenberg's uncertainty principle.
- Collection of individual atom is not possible.
- Electron density in an atom is affected by neighbouring atoms.

○ **Covalent radius** : It is defined as the half of the internuclear distance between the two atoms held by means of single covalent bond in a molecule.

- For a homonuclear diatomic molecule, covalent radius = $\frac{1}{2}$ [bond length]
- For heteronuclear diatomic molecule covalent radius = $r_A + r_B$ (if atoms have same electronegativities) and covalent radius = $r_A + r_B - 0.09 (\chi_A - \chi_B)$ (if atoms have different electronegativities)

○ **van der Waals' radius** : It is defined as the half of the distance between the nuclei of two non bonded isolated atoms or two adjacent atoms belonging to two neighbouring molecules of an element in the solid state.

○ **Metallic radius** : It is defined as half the distance between two successive nuclei of two adjacent metal atoms in the metallic closed packed crystal lattice.

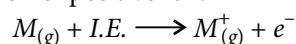
○ **Ionic radius** : It is the distance of the outermost shell of an anion or cation from its nucleus.

- Size of a cation is always less than that of the parent atom whereas size of anion is always greater than the parent atom.
- In case of isoelectronic ions, the size decreases with increase in the nuclear charge.

➤ Atomic radius increases down the group as new valence shells are added.

➤ In general, atomic radii decreases with increase in atomic number as we move from left to right in a period (except for noble gases).

❑ **Ionisation enthalpy** : It is defined as the amount of energy required to remove an electron from an isolated gaseous atom of an element resulting in the formation of positive ion.



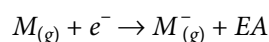
○ **Factors affecting ionisation enthalpy** :

- **Size of atom** : $I.E. \propto \frac{1}{\text{Size of atom}}$
- **Nuclear charge** : $I.E. \propto \text{Nuclear charge}$
- **Screening effect** : $I.E. \propto \frac{1}{\text{Screening effect}}$
- **Completely filled or half-filled orbitals** : It is comparatively difficult to remove the electrons from these orbitals (being more stable).
- **Type of electrons involved** : Ionisation energy decreases in the order of $s > p > d > f$ -orbitals.

➤ Ionisation energy decreases down the group due to increase in size of the atom and screening effect of intervening electrons.

➤ First ionisation enthalpy increases along a period from left to right as the charge on nucleus increases while valence shell remains the same leading to increase in effective nuclear charge.

❑ **Electron gain enthalpy** : It is the amount of energy released when an electron is added to an isolated gaseous atom.



○ **Factors affecting electron gain enthalpy** :

- **Size of the atom** : $\Delta_{eg}H \propto \frac{1}{\text{Size of atom}}$
- **Nuclear charge** : $\Delta_{eg}H \propto \text{Effective nuclear charge}$
- **Screening effect** : $\Delta_{eg}H \propto \frac{1}{\text{Screening effect}}$

➤ Electron gain enthalpy becomes less negative as we move down the group.

➤ Electron gain enthalpy becomes more and more negative from left to right in a period (except for noble gases).

SELF CHECK

- The ionic radii (in Å) of N^{3-} , O^{2-} and F^- are respectively
(a) 1.71, 1.40 and 1.36 (b) 1.71, 1.36 and 1.40
(c) 1.36, 1.40 and 1.71 (d) 1.36, 1.71 and 1.40
(JEE Main 2015)
- The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^+ will be
(a) + 2.55 eV (b) - 2.55 eV
(c) - 5.1 eV (d) - 10.2 eV
(JEE Main 2013)
- Which of the following represents the correct order of increasing first ionisation enthalpy for Ca, Ba, S, Se and Ar?
(a) $Ca < Ba < S < Se < Ar$
(b) $Ca < S < Ba < Se < Ar$
(c) $S < Se < Ca < Ba < Ar$
(d) $Ba < Ca < Se < S < Ar$ (JEE Main 2013)

□ **Electronegativity** : It is defined as the relative tendency of an atom to attract the shared pair of electrons towards itself.

- Mulliken scale of electronegativity

$$\chi = \frac{1}{2} [\Delta_i H + \Delta_{eg} H]$$

- Pauling scale of electronegativity

$$\chi_A - \chi_B = 0.1017 \sqrt{\Delta}$$

$$\text{where, } \Delta = E_{A-B} - \frac{1}{2} \sqrt{E_{A-A} + E_{B-B}}$$

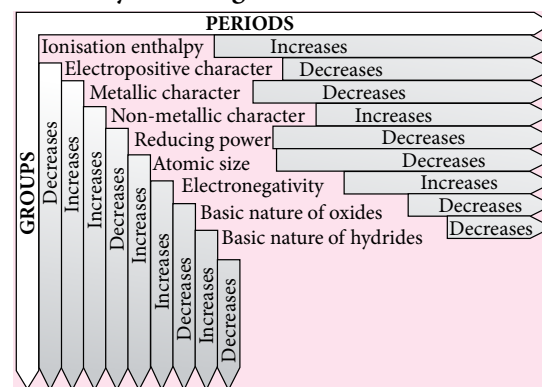
Here, E represents bond dissociation enthalpy (in kJ mol^{-1}).

- Electronegativity decreases on moving down the group and increases along a period.
- **Valency** : The combining capacity of an element is termed as its valency *i.e.*, the number of electrons present in the outermost shell of the atom which are required for bonding.
- Valency of the elements increases from 1 to 4 and then decreases from 4 to 0 in a period *w.r.t.* hydrogen or oxygen.
 - When we move down the group, the number of valence electrons remains the same therefore, all the elements in a group exhibit the same valency.
- **Chemical reactivity** :
- Chemical reactivity is high at the two extremes of the periodic table and lowest in the centre.

- The high chemical reactivity of alkali metals on the extreme left is due to their ability to lose an electron while that of halogens on the right side is due to their high tendency to gain an electron.

- Basic nature of oxides of the elements decreases and the acidic nature increases along a period while down the group basic nature increases and acidic nature decreases.
- Strength of oxyacids of non-metals increases along a period and decreases down the group.
- The nature of hydrides changes from basic to acidic from left to right in a period while the acidic nature of the hydrides of non-metals increases down the group.

□ **Summary of some general trends :**



KEY POINT

- The difference between actual nuclear charge and the effective nuclear charge is called screening constant.
- Effective nuclear charge, $Z^* = Z - \sigma$ where σ is Slater's screening constant and Z is the atomic number.
- For one electron system, $\sigma = 0$
- The electron gain enthalpy of first member of representative element group is less negative than the second member because of small size as a result of which it has strong electron-electron repulsions.
- Percentage ionic character

$$= 16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2$$
 - If $\chi_A - \chi_B = 1.7$, bond is 50% covalent and 50% ionic.
 - If $\chi_A - \chi_B > 1.7$, bond is predominately ionic.
 - If $\chi_A \approx \chi_B$, $A - B$ bond is purely covalent.

SELF CHECK

4. Which one of the following orders presents the correct sequence of the increasing basic nature of the given oxides?
- $\text{Al}_2\text{O}_3 < \text{MgO} < \text{Na}_2\text{O} < \text{K}_2\text{O}$
 - $\text{MgO} < \text{K}_2\text{O} < \text{Al}_2\text{O}_3 < \text{Na}_2\text{O}$
 - $\text{Na}_2\text{O} < \text{K}_2\text{O} < \text{MgO} < \text{Al}_2\text{O}_3$
 - $\text{K}_2\text{O} < \text{Na}_2\text{O} < \text{Al}_2\text{O}_3 < \text{MgO}$ (AIEEE 2011)

GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF METALS

- Modes of Occurrence of Elements
- Extraction of Al, Fe, Cu and Zn
- Thermodynamic and Electrochemical Principles Involved in the Extraction of Metals.

TIPS TO REMEMBER

Modes of Occurrence of Elements

- Native state** : Least reactive elements like noble gases and noble metals occur in free state or native state.

- Combined state** : Highly reactive elements like fluorine, chlorine, sodium etc. are found in combined state.

Steps Involved in the Extraction

- The entire process of extracting metals from their ores is called *metallurgy* and it involves four main steps :
 - Concentration of ore** : Removal of gangue from ore is known as concentration or dressing of ore.
 - Depending upon the nature of the ore and the impurities present, different methods are used for concentration of ore.

Method	Principle and ores specification	Process
Hydraulic washing	It is based on the difference in the specific gravities of the gangue and the ore particles and is mostly used for oxide ores.	The powdered ore is agitated with water. The heavier ore particles settle down while lighter impurities are washed away.
Electromagnetic separation	It is based on the difference in magnetic properties of the gangue and ore particles and is used for magnetite (Fe_3O_4), haematite (Fe_2O_3), wolframite (FeWO_4), chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) etc.	The powdered ore containing impurity is dropped on a belt which rotates around a magnetic roller. The magnetic particles fall nearer to the roller while non-magnetic particles fall farther off.
Froth floatation process	It is based on the difference in wetting properties of gangue and ore particles and is mostly used for sulphide ores.	Powdered ore is mixed with pine oil and water and violently agitated with air. Ore particles rise to the surface in the form of froth and impurities remain in water.
Leaching	It is based on the difference in chemical properties of gangue and ore particles and is used for extraction of Au, Ag and pure alumina from bauxite ore.	<p>Baeyer's process :</p> $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} + \text{H}_2\text{O} \longrightarrow 2\text{Na}[\text{Al}(\text{OH})_4]$ $2\text{Na}[\text{Al}(\text{OH})_4] + 2\text{CO}_2 \longrightarrow \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O} + 2\text{NaHCO}_3$ $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O} \xrightarrow{1200^\circ\text{C}} \text{Al}_2\text{O}_3 + x\text{H}_2\text{O}$ <p>Mac Arthur Forest cyanide process :</p> $4\text{Ag} + 8\text{NaCN} + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 4\text{Na}[\text{Ag}(\text{CN})_2] + 4\text{NaOH}$ $2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Zn} \longrightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Ag} \downarrow$

- **Extraction and isolation of metals :**
 - **Calcination :** It is the process of heating the ore strongly below its melting point either in the absence of air or in the limited supply.
 - Calcination is carried out in case of carbonate and hydrated oxide ores, which lose carbon dioxide, moisture and volatile impurities.
 - **Roasting :** It is the process of heating the ore strongly below the melting point in a sufficient supply of air to bring about its oxidation and remove volatile impurities.
 - Roasting is generally carried out in a reverberatory furnace or a blast furnace in case of sulphide ores.
- **Reduction or conversion of ores to metals :** The ore obtained after calcination or roasting is reduced to metal and choice of reducing agent depends upon the nature of ore.
 - Carbon or carbon monoxide is used for oxides of Fe, Cu, Zn, Mg, Co etc.
 - Electropositive metals like Na, Al, Mg or hydrogen are used for reduction of ores of Mn, Cr, Ti, Mo, W etc.
 - Water gas is used for nickel ores.
 - Autoreduction process is used for ores of Pb, Hg, Cu etc.
 - Electrolytic reduction is used for highly electropositive metals.
 - Hydrometallurgy or displacement method is used for Ag, Au etc.
- **Refining of metals :** Purification of crude metals by removing the impurities present in it is called refining.
 - Different methods are used depending upon the differences in properties of the metal and the impurity.

Refining/Purification of the Crude Metal

Methods	Metals purified
Liquation	Used for low melting metals like Sn, Pb, Hg, Bi, etc.
Distillation	Used for volatile metals like Zn, Hg, Cd, etc. or metals containing non-volatile impurities.

Poling	Used for metals which contain impurities of their own oxides. e.g. Cu.
Cupellation	Used for metals containing easily oxidisable impurities. e.g., Ag containing Pb impurities.
Electrolytic refining	Used for metals like Cu, Ag, Au, Al which get deposited at cathode and impurities get deposited at anode. Solution of a soluble metal salt acts as the electrolyte.
Mond's process	Used for refining of Ni. $4\text{CO} + \underset{\text{Impure}}{\text{Ni}} \xrightarrow{60^\circ-80^\circ\text{C}} \text{Ni(CO)}_4 \downarrow$ $\text{Ni} + 4\text{CO} \xleftarrow{180^\circ\text{C}} \text{Pure}$
Zone refining	Used to produce extremely pure metals (semiconductors) like Si, Ge, Ga, B and In.
van Arkel method	Used for ultra-pure metals like Ti, Zr which are used in space technology. $\underset{\text{Impure}}{\text{Ti}_{(s)}} + 2\text{I}_{2(g)} \xrightarrow{523\text{ K}} \text{TiI}_{4(g)} \xrightarrow{1673\text{ K}} \underset{\text{Pure}}{\text{Ti}_{(s)}} + 2\text{I}_{2(g)}$ $\underset{\text{Impure}}{\text{Zr}} + 2\text{I}_2 \xrightarrow{870\text{ K}} \text{ZrI}_{4(g)} \xrightarrow{1800\text{ K}} \underset{\text{Pure}}{\text{Zr}_{(s)}} + 2\text{I}_{2(g)}$

SELF CHECK

- Sulphide ores are common for the metals
 - Ag, Cu and Pb
 - Ag, Cu and Sn
 - Ag, Mg and Pb
 - Al, Cu and Pb (JEE Advanced 2013)
- In the cyanide extraction process of silver from argentite ore, the oxidising and reducing agents used are
 - O₂ and CO respectively
 - O₂ and Zn dust respectively
 - HNO₃ and Zn dust respectively
 - HNO₃ and CO respectively.

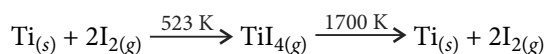
(IIT-JEE 2012)

Extraction of Fe, Cu, Al and Zn

Extraction of Al	Extraction of Fe
<p>Ores : Bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) Cryolite ($\text{Na}_3\text{AlF}_6$)</p> <p>Concentration : (Leaching) $\text{Al}_2\text{O}_3 + 2\text{NaOH} \rightarrow 2\text{NaAlO}_2 + \text{H}_2\text{O}$ $\text{NaAlO}_2 + 2\text{H}_2\text{O} \rightarrow \text{NaOH} + \text{Al}(\text{OH})_3$ $2\text{Al}(\text{OH})_3 \xrightarrow{\Delta} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$ Pure</p> <p>Electrolytic reduction (Hall and Heroult process) : Pure Al_2O_3 + cryolite (electrolyte) $\text{Al}_2\text{O}_3 \rightarrow 2\text{Al}^{3+} + 3\text{O}^{2-}$; $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$</p> <p>Purification : (Hoope's process)</p>	<p>Ores : Haematite (Fe_2O_3)</p> <p>Concentration : (Electromagnetic separation)</p> <p>Calcination and roasting : (Removal of H_2O, S, C and As) $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \rightarrow 2\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$ $\text{FeCO}_3 \rightarrow \text{FeO} + \text{CO}_2$ $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$ $4\text{As} + 3\text{O}_2 \rightarrow 2\text{As}_2\text{O}_3$ $2\text{Fe} + \frac{3}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$</p> <p>Smelting : (Blast furnace) $\text{Fe}_2\text{O}_3 + 3\text{CO} \xrightarrow{400-700^\circ\text{C}} 2\text{Fe} + 3\text{CO}_2$ $\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$; $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3(\text{slag})$ $2\text{CO} \xrightarrow{\text{Hot iron}} \text{CO}_2 + \text{C}$; $\text{SiO}_2 + 2\text{C} \xrightarrow{1200^\circ\text{C}} \text{Si} + 2\text{CO}$ $\text{MnO}_2 + 2\text{C} \rightarrow \text{Mn} + 2\text{CO}$; $\text{P}_4\text{O}_{10} + 10\text{C} \rightarrow 4\text{P} + 10\text{CO}$ Pig iron so formed is then remelted and cooled to form cast iron.</p> <p>Purification : By oxidising impurities in reverberatory furnace lined with haematite. $\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO}$</p>
Extraction of Zn	Extraction of Cu
<p>Ores : (i) Zinc blende : ZnS (ii) Calamine : ZnCO_3 (iii) Zincite : ZnO</p> <p>Concentration : (Froth floatation method)</p> <p>Roasting : $2\text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + 2\text{SO}_2$ $\text{ZnS} + 2\text{O}_2 \rightarrow \text{ZnSO}_4$ $2\text{ZnSO}_4 \xrightarrow{\Delta} 2\text{ZnO} + 2\text{SO}_2 + \text{O}_2$</p> <p>Reduction : $\text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO}$ Electrolytic refining, distillation</p> <p>Purification : Electrolytic refining, distillation</p>	<p>Ores : Copper pyrites (CuFeS_2)</p> <p>Concentration : (Froth floatation method)</p> <p>Roasting : $2\text{CuFeS}_2 + \text{O}_2 \rightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2 \uparrow$</p> <p>Smelting : Sand + coke $2\text{FeS} + 3\text{O}_2 \rightarrow 2\text{FeO} + 2\text{SO}_2$ $\text{FeO} + \text{SiO}_2 \rightarrow \text{FeSiO}_3(\text{slag})$</p> <p>Bessemerisation : Sand + hot blast of air $2\text{Cu}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$ $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6\text{Cu} + \text{SO}_2$ The copper so obtained upon bessemerisation is called <i>blister copper</i>.</p> <p>Purification : Blister copper can be purified by poling or electrolytic refining to get pure copper.</p>

SELF CHECK

7. Which method of purification is represented by the following equation?



- (a) Cupellation (b) Poling
(c) van Arkel (d) Zone refining

(AIEEE 2012)

Thermodynamic and Electrochemical Principles of Extraction

Thermodynamic Principles :

- Thermodynamics help in understanding the conditions of temperature and selecting suitable reducing agent in a metallurgical process.
- *Gibb's Helmholtz equation* is used to check the feasibility of a reduction process.
 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, if $\Delta G^\circ < 0$, the reduction is feasible.
- For a reaction, enthalpy change is fixed but temperature factor can be controlled and it can be the deciding factor for feasibility of that reaction.

❑ **Coupled reactions :** If reactants and products of two reactions are put together in a system and the net ΔG of two possible reactions is -ve, the overall reaction will take place. These reactions are called coupled reactions.

❑ **Ellingham diagram :** It consists of plots of $\Delta_f G^\circ$ vs. temperature for the formation of oxides of elements.

- It provides a sound idea about selecting a reducing agent in reduction of oxides.
- Such diagrams help in predicting the feasibility of thermal reduction of an ore. ΔG must be -ve at a given temperature for a reaction to be feasible.

Electrochemical principles :

- Electrolysis is used to carry out the reduction of a molten metal salt.
- The electrochemical principles of this method can be understood through the equation, $\Delta G^\circ = -nFE^\circ$
- More reactive metals have large negative values of the electrode potential so, their reduction is difficult.
- If the difference of two E° values corresponds to a positive E° and consequently negative ΔG° , then the less reactive metal will come out of the solution and the more reactive metal will go to the solution.

KEY POINT

- Nitrate ores are rare because all nitrates are water soluble and they decompose at higher temperature into oxide or metal.
- In froth floatation process, *collectors* such as pine oil, fatty acids, xanthates etc. enhance non wettability of the mineral particles, *froth stabilisers* like cresols, aniline etc. stabilise the froth and *depressants* like NaCN are added to separate two sulphide ores.
- Materials which can sustain very high temperature and remain chemically inert are used for making inner lining of furnaces and are called refractory materials.
- Acidic refractory materials—silica, quartz.
- Basic refractory materials—lime, dolomite, magnesite.
- Neutral refractory materials—graphite, chromite, bone ash, bauxite, alumina.

HYDROGEN

- Position of Hydrogen in Periodic Table
- Isotopes of Hydrogen
- Preparation, Properties and Uses of Hydrogen
- Physical and Chemical Properties of Water and Heavy Water
- Hydrogen Peroxide
- Hydrides
- Hydrogen as a Fuel

TIPS TO REMEMBER

Position of Hydrogen in the Periodic Table

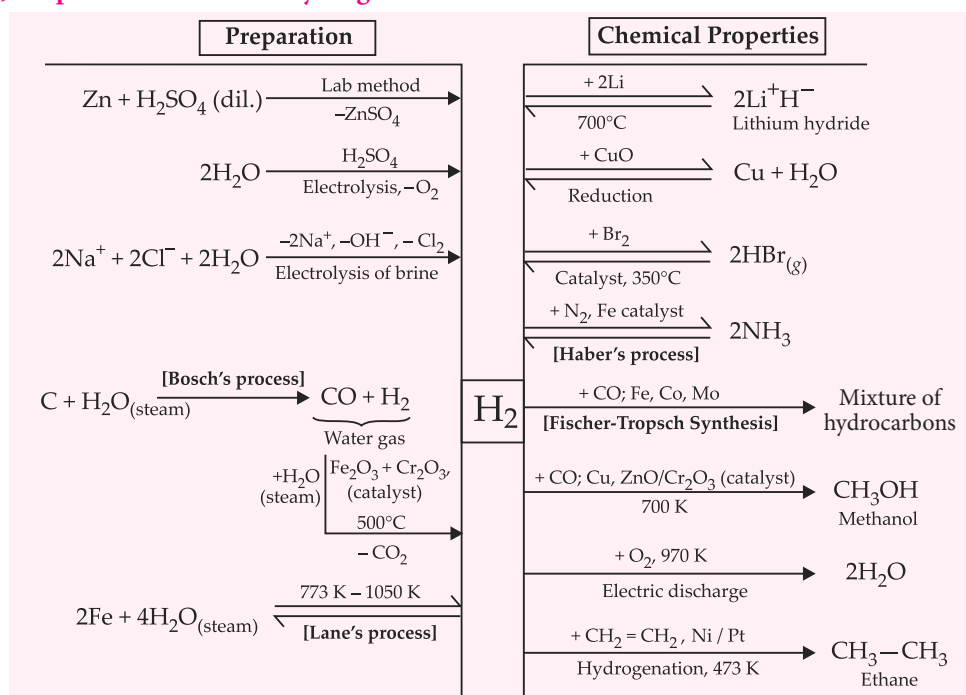
- ❑ $H_1^{1.008}$: Electronic configuration $-1s^1$
- ❑ Hydrogen is the first element of the periodic table and its position is anomalous.
- ❑ It resembles alkali metals w.r.t. electronic configuration, electropositive character, valency and oxidation state, combination with electronegative elements and liberation at cathode.
- ❑ It resembles halogens w.r.t. electronic configuration (one electron less than the nearest noble gas configuration), ionisation energy, electronegative character, oxidation state, diatomic nature and liberation at anode.

Isotopes of Hydrogen

- Hydrogen has three isotopes with mass number 1, 2 and 3 respectively. These are called protium, deuterium and tritium.

Name	Symbol	Relative abundance
Protium or hydrogen	${}^1_1\text{H}$ or H	99.98%
Deuterium	${}^2_1\text{H}$ or D	0.016%
Tritium	${}^3_1\text{H}$ or T	10–15% (Radioactive)

Preparation, Properties and Uses of Hydrogen



Uses :

- As a reducing agent in the laboratory and industry.
- In the hydrogenation of vegetable oils.
- In the atomic-hydrogen torch for welding purposes in which temperature of the order of 4000°C is required.
- As a rocket fuel in the form of liquid hydrogen and liquid oxygen.
- In the manufacture of synthetic petrol.
- In the preparation of many compounds such as ammonia, water gas, methanol and fertilizers such as urea, ammonium sulphate, etc.

KEY POINT

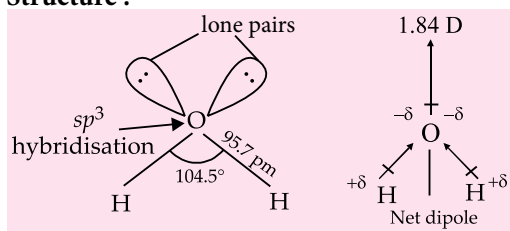
- Pure zinc is not used in the preparation of dihydrogen because its reaction with sulphuric acid is slow. The presence of some impurities increases the rate of reaction due to the formation of electrochemical couples.
- Concentrated sulphuric acid is also not used for the preparation of dihydrogen because zinc reacts with concentrated acid to form SO_2 gas instead of dihydrogen.

$$\text{Zn} + 2\text{H}_2\text{SO}_{4(\text{conc.})} \longrightarrow \text{ZnSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$$
- H_2 has two nuclear spin isomers—when spins of both protons in hydrogen molecule are in the same direction it is called *ortho*-hydrogen and when the proton spins are in the opposite direction it is called *para*-hydrogen.
- Ordinary hydrogen is an equilibrium mixture of *ortho*- and *para*-hydrogen.
- Nascent hydrogen or newly born hydrogen is more reactive and more powerful reducing agent than ordinary hydrogen.

Water

- Water is the principal constituent of earth's surface.

Structure :



Physical properties :

- The freezing point, boiling point, heat of fusion and heat of vaporisation of water are higher as compared to the hydrides of other members of the same group (16) such as H₂S, H₂Se, H₂Te etc. due to the presence of hydrogen bonding in H₂O molecules.
- Water has capacity to dissolve most of the inorganic substances and a few organic substances such as urea, alcohol, sugar etc. and is, therefore, regarded as a universal solvent.

Chemical properties :

- $\text{H}_2\text{O}_{(l)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{OH}^-_{(aq)}$
(Self-ionisation of water)
- $\text{H}_2\text{O}_{(l)} + \text{HCl}_{(aq)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{Cl}^-_{(aq)}$
Base Acid Acid Base
- $\text{H}_2\text{O}_{(l)} + \text{NH}_3_{(aq)} \rightleftharpoons \text{NH}_4^+_{(aq)} + \text{OH}^-_{(aq)}$
Acid Base Acid Base
(Amphoteric character)
- $2\text{Na}_{(s)} + 2\text{H}_2\text{O}_{(l)} \xrightarrow[\text{Oxidation}]{\text{Reduction}} 2\text{NaOH} + \text{H}_{2(g)}$
(As an oxidising agent)
- $n\text{CO}_{2(g)} + n\text{H}_2\text{O}_{(l)} \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} (\text{CH}_2\text{O})_n + \text{O}_{2(g)}$
Carbohydrate
(As reducing agent)

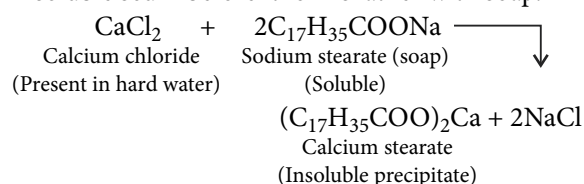
Heavy Water

- Discovered by Urey.
- Heavy water is obtained from ordinary water by prolonged electrolysis.
- Physical properties :**
 - It is colourless, odourless and tasteless liquid.
 - Nearly all physical constants of heavy water are higher than the corresponding values of ordinary water.
- Chemical properties :**
 - $2\text{D}_2\text{O} + 2\text{Na} \longrightarrow 2\text{NaOD} + \text{D}_2$
Heavy hydrogen

- $\text{Na}_2\text{O} + \text{D}_2\text{O} \longrightarrow 2\text{NaOD}$
Deutero sodium hydroxide
- $\text{SO}_3 + \text{D}_2\text{O} \longrightarrow \text{D}_2\text{SO}_4$
Deutero sulphuric acid
- $\text{Al}_4\text{C}_3 + 12\text{D}_2\text{O} \longrightarrow 3\text{CD}_4 + 4\text{Al(OD)}_3$
Aluminium carbide Deutero methane
- $\text{CaC}_2 + 2\text{D}_2\text{O} \longrightarrow \text{DC}\equiv\text{CD} + \text{Ca(OD)}_2$
Calcium carbide Deutero ethyne

Hard and Soft Water

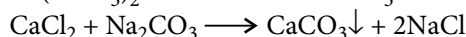
- Water is said to be soft if it produces sufficient lather with soap while it is said to be hard if it forms an insoluble scum before it forms lather with soap.



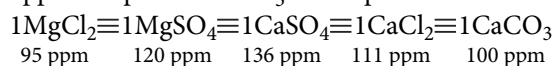
Hardness of water :

- Temporary :** When hardness of water is due to the presence of bicarbonates of Mg and Ca. It can be removed by boiling.
- Permanent :** When hardness of water is due to the presence of sulphates or chlorides of Ca and Mg. It cannot be removed by boiling.

Both temporary and permanent hardness can be removed by adding caustic soda (NaOH).



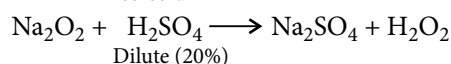
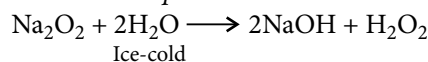
Degree of hardness is the number of parts of CaCO₃ present in a million (10⁶) parts of water by weight *i.e.*, 1ppm = 1 part of CaCO₃ in 10⁶ parts of water.



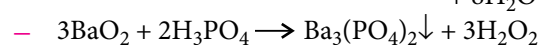
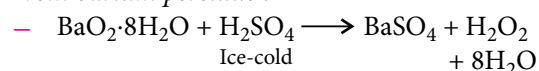
Hydrogen Peroxide (or Oxygenated Water)

Preparation :

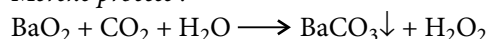
- From sodium peroxide :**



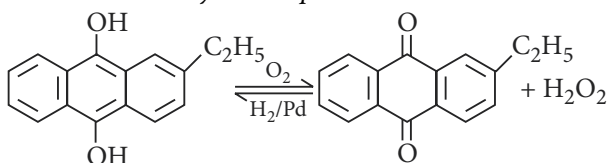
- From barium peroxide :**



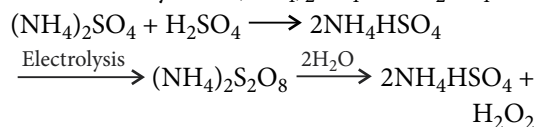
- Merck's process :**



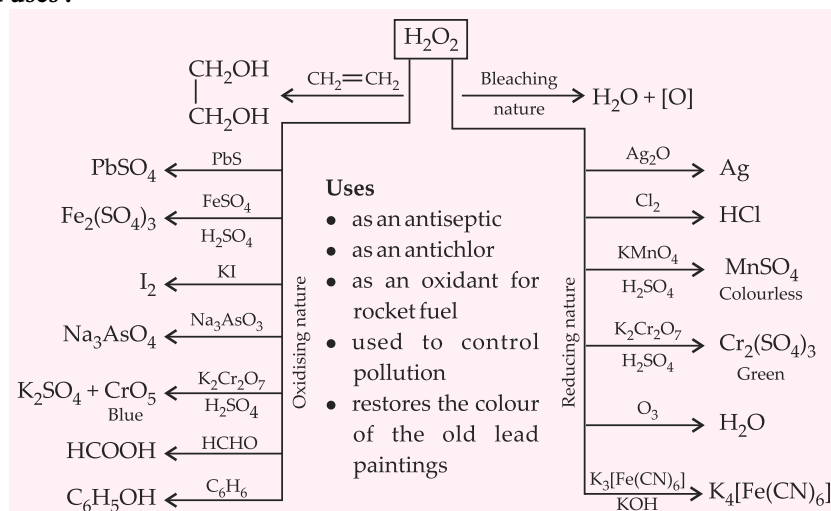
○ From 2-ethylanthraquinol :



○ From electrolysis of $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 :

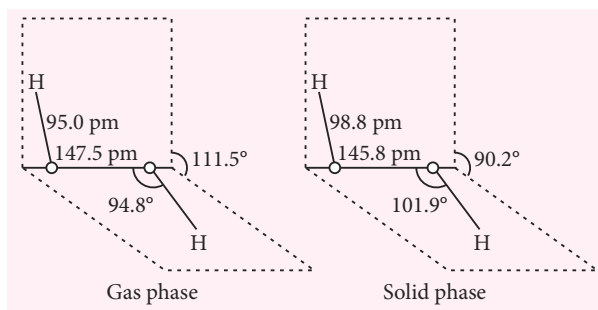


Reactions and uses :



Structure :

○ H_2O_2 has an open book like (non-planar) structure.



KEYPOINT

- Deutero compounds have higher boiling and melting points than protium compounds.
- In the preparation of H_2O_2 from barium peroxide, phosphoric acid is preferred over sulphuric acid since H_2SO_4 acts as a catalyst for decomposition of H_2O_2 .
- Concentration of H_2O_2 is expressed in terms of volume strength.
 - 10 volume of H_2O_2 solution means 1 mL of this solution on decomposition evolves 10 mL of O_2 at NTP.

- ‘10 volume’ solution of H_2O_2 is 3.035% solution.
- Strength of ‘10 volume’ H_2O_2 solution is 30.35 g/litre.
- Volume strength = $5.6 \times \text{Normality}$
- Volume strength = $11.2 \times \text{Molarity}$

SELF CHECK

8. The molecular formula of a commercial resin used for exchanging ions in water softening is $\text{C}_8\text{H}_7\text{SO}_3\text{Na}$ (Mol. wt. 206). What would be the maximum uptake of Ca^{2+} ions by the resin when expressed in mole per gram resin?

- (a) $\frac{2}{309}$ (b) $\frac{1}{412}$
 (c) $\frac{1}{103}$ (d) $\frac{1}{206}$

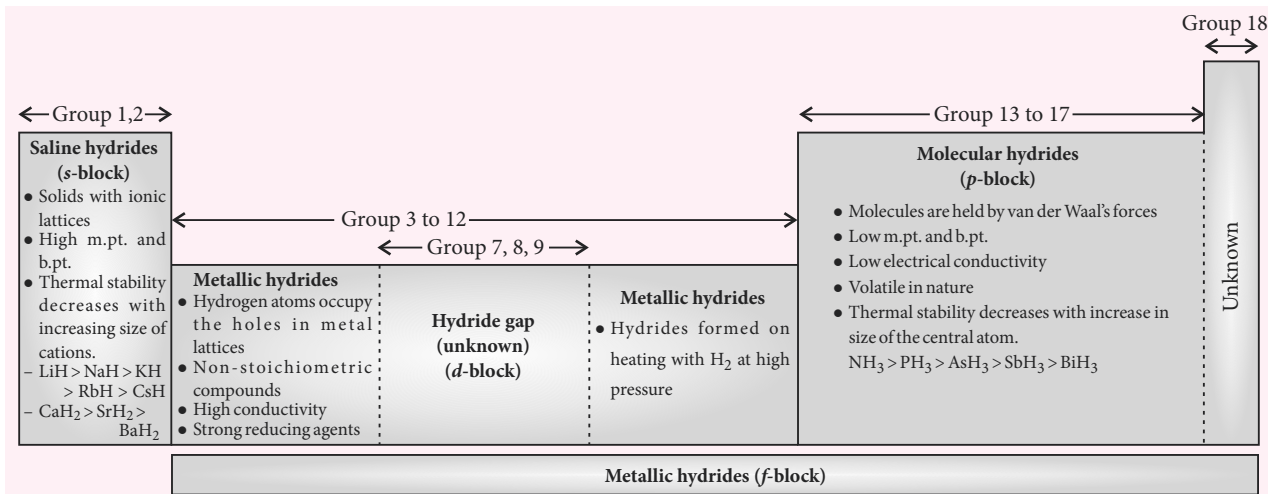
(JEE Main 2015)

9. From the following statements regarding H_2O_2 , choose the incorrect statement.

- (a) It has to be stored in plastic or wax lined glass bottles in dark.
 (b) It has to be kept away from dust.
 (c) It can act only as an oxidising agent.
 (d) It decomposes on exposure to light.

(JEE Main 2015)

Hydrides



Hydrogen as a Fuel

- Hydrogen has been selected as the best alternate of fossil fuels as H_2 is very abundant in water.
- Hydrogen is environmentally clean fuel because it gives water on combustion.
- Hydrogen has highest calorific value.

s-BLOCK ELEMENTS

- General Properties of Alkali Metals and Alkaline Earth Metals
- Anomalous Behaviour of the First Element
- Diagonal Relationship
- Preparation, Properties and Uses of Some Important Compounds
- Biological Significance of Na, K, Mg and Ca

TIPS TO REMEMBER

- Elements of group 1 or IA (alkali metals) and group 2 or IIA (alkaline earth metals) constitute s-block elements.

Alkali Metals

Property	Li	Na	K	Rb	Cs
At. no. (Z)	3	11	19	37	55
Electronic configuration	[He] $2s^1$	[Ne] $3s^1$	[Ar] $4s^1$	[Kr] $5s^1$	[Xe] $6s^1$
Flame colouration	Crimson red	Golden yellow	Pale violet	Reddish violet	Blue

Physical properties :

- Lower densities than other metals.
- One loosely bound valence electron.
- Largest atomic radii in their periods.

- Low ionisation energies result in their metallic properties and high reactivities.
- They react readily with non-metals, particularly halogens.

Chemical properties :

Alkali Metals	Reaction with H_2O	$\rightarrow \text{MOH} + \frac{1}{2}\text{H}_2$
	Reaction with O_2	$\rightarrow \text{Li}_2\text{O}, \text{Na}_2\text{O}_2, \text{KO}_2$
	Reaction with H_2	$\rightarrow \text{MH}$
	Reaction with group 15 elements	$\rightarrow \text{M}_3\text{P}, \text{M}_3\text{As}, \text{M}_3\text{Sb}$
	Reaction with group 16 elements	$\rightarrow \text{M}_2\text{S}, \text{M}_2\text{Se}, \text{M}_2\text{Te}$
	Reaction with halogens	$\rightarrow \text{MF}, \text{MCl}, \text{MBr}, \text{MI}$
	Reaction with ammonia	$\rightarrow \text{MNH}_2 + \frac{1}{2}\text{H}_2$
	Reaction with N_2	$\rightarrow \text{Li}_3\text{N}$ (only Li reacts)
	Reaction with C	$\rightarrow \text{Li}_2\text{C}_2$ (only Li reacts)

General Trends in Properties of Alkali Metals

Atomic radii	Li	M.p. and b.p.	max
Atomic volume	Na	Hardness	
Density	K	Ionisation energy	
Radioactivity	Rb	Conductivity	
Reducing power	Cs	Electronegativity	
Electropositivity		Solubility of salts having large anions	
Anion stabilisation			
Solubility of salts having small anions			
	max		

❑ **Anomalous behaviour of lithium :**

- Forms only monoxide.
- Reacts with N_2 .
- Carbonate, nitrate, and hydroxide decompose on heating.
- Salts are sparingly soluble in water.
- Does not form alums.

❑ **Diagonal relationship of Li with Mg :**

- Both are hard and ductile.

○ $LiOH$ and $Mg(OH)_2$ are weak bases.

○ Bicarbonates of both do not exist in solid state.

○ Both produce nitrides on reacting with N_2 gas.

○ Carbonates, nitrates, hydroxides of both are unstable to heat.

○ Nitrates of both give NO_2 , O_2 and metal oxides.

○ Both do not produce alums.

Some Important Compounds

Compound	Preparation	Properties	
		Physical	Chemical
Sodium hydroxide or caustic soda ($NaOH$)	Electrolytic process in mercury cathode cell $2NaCl_{(aq)} + 2H_2O_{(l)} \longrightarrow \underbrace{H_{2(g)}}_{\text{At cathode}} + \underbrace{Cl_{2(g)} + 2NaOH_{(aq)}}_{\text{At anode}}$	$NaOH$ is deliquescent, white crystalline solid. $NaOH$ dissolves readily in water to yield highly alkaline solution which is corrosive, soapy in touch and bitter in taste.	$Na_2CO_3 \xleftarrow{CO_2} HCOONa \xleftarrow{CO} SO_2 \xleftarrow{S, \Delta} Na_2S_2O_3 \xleftarrow{P_4} NaH_2PO_2 \xleftarrow{+ PH_3} NaMO_2 \xleftarrow{M(M=B, Al)} NaOH$ $NaX \xleftarrow{X_2 \text{ (Hot)}} NaXO_3 + H_2O \xleftarrow{NH_3 \uparrow} NH_4Cl + NaCl + H_2O$ $X_2 \text{ (Cold)} \xrightarrow{NaX + NaXO + H_2O} Zn \text{ or } ZnO_2 \xrightarrow{Na_2ZnO_2} SiO_2 \xrightarrow{Na_2SiO_3} Al_2O_3 \text{ or } Al(OH)_3 \xrightarrow{Sn} NaAlO_2 \xrightarrow{ZnSO_4} Zn(OH)_2 \xrightarrow{NaOH} Na_2ZnO_2 \xrightarrow{FeCl_3} Fe(OH)_3 \downarrow + NaCl$
Sodium carbonate or washing soda ($Na_2CO_3 \cdot 10H_2O$)	Sodium carbonate is manufactured by <i>Solvay process</i> . Sodium bicarbonate being sparingly soluble, crystallises out. This is finally calcined to form sodium carbonate. $Na^+ + Cl^- + NH_4^+ + OH^- + CO_2 \longrightarrow Na^+ + HCO_3^- + NH_4^+ + Cl^-$ $Na^+ + HCO_3^- \longrightarrow NaHCO_3 \text{ (as precipitate)}$ $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$	Sodium carbonate is a white crystalline solid which readily dissolves in water. Its solubility decreases with increase of temperature.	$2NaHCO_3 \xleftarrow{CO_2} Na_2SiO_3 \xleftarrow{SiO_2} Na_2CO_3 \cdot 10H_2O \xrightarrow{H_2O} 2NaOH + H_2CO_3$ $Na_2CO_3 \cdot 10H_2O \xrightarrow{HCl} NaCl + H_2O + CO_2$ $Na_2CO_3 \cdot 10H_2O \xrightarrow{SO_2} Na_2SO_3 + CO_2$ $Na_2CO_3 \cdot 10H_2O \xrightarrow{H_2O, S} Na_2S_2O_3$
Sodium hydrogen carbonate or baking soda ($NaHCO_3$)	Obtained as an intermediate product in <i>Solvay process</i> . $NaCl + NH_3 + CO_2 + H_2O \longrightarrow NaHCO_3 + NH_4Cl$ It can also be prepared by passing CO_2 through solution of sodium carbonate. $Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$	It is a white crystalline powder and less soluble than sodium carbonate.	$NaHCO_3$ on heating decomposes to produce bubbles of CO_2 which make the cakes and pastries fluffy. $2NaHCO_3 \xrightarrow[100^\circ C]{\Delta} Na_2CO_3 + H_2O + CO_2$ It is amphiprotic <i>i.e.</i> , it can act as H^+ donor as well as H^+ acceptor. $HCO_3^- + H^+ \rightleftharpoons H_2CO_3;$ $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

Biological Significance of Na and K

- Na^+ and K^+ are essential for proper functioning of human body.
 - Different ratio of Na^+ to K^+ inside and outside cells produce an electrical potential across the cell membrane which is essential for functioning of nerve and muscle cells.
 - These ions activate many enzymes.
 - These ions primarily help in transmission of nerve signals, in regulating the flow of water across cell membranes, transport of sugars and amino acids into the cells etc.

KEY POINT

- Alkali metals are strong reducing agents hence, cannot be extracted by reduction of their oxides and other compounds.
- On heating, colourless alkali halides become coloured and colour of most of the alkali metal halides resembles with colour of flame imparted by that alkali metal.
- **Basic strength:** $\text{LiOH} < \text{NaOH} < \text{KOH} < \text{RbOH} < \text{CsOH}$
- **Stability:** $\text{Li}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{K}_2\text{CO}_3 < \text{Rb}_2\text{CO}_3 < \text{Cs}_2\text{CO}_3$

Group-2 Elements (Alkaline Earth Metals)

Property	Be	Mg	Ca	Sr	Ba	Ra
At. no. (Z)	4	12	20	38	56	88
Electronic configuration	$[\text{He}] 2s^2$	$[\text{Ne}] 3s^2$	$[\text{Ar}] 4s^2$	$[\text{Kr}] 5s^2$	$[\text{Xe}] 6s^2$	$[\text{Rn}] 7s^2$
Flame colouration	None	None	Brick red	Crimson	Grassy green	Crimson

Physical properties :

Atomic and ionic radii	Smaller than corresponding alkali metals and increase down the group
Ionisation enthalpy	Higher than corresponding alkali metals and decreases down the group
Electropositive or metallic character	Less electropositive or metallic than alkali metals and electropositive or metallic character increases down the group

Electronegativity	Higher than corresponding alkali metals and decreases down the group
Physical state	All are silvery white when freshly cut, light, malleable and soft but harder than alkali metals
Melting and boiling points	Higher than alkali metals and do not show any regular trend because of different crystal structures adopted by different metals
Density	Denser, heavier and harder than alkali metals and density decreases from Be to Ca and then increases
Conductance	Good conductors of heat and electricity
Specific heats	Greater than alkali metals and do not show regular trend
Oxidation number and valency	All form divalent cations and exhibit +2 oxidation state
Reducing character	Increases from Be to Ba
Colour and magnetic properties of salts	Divalent salts are diamagnetic and colourless if anion is colourless

Chemical properties :

Alkaline Earth Metals	Reaction with H_2O	$\text{M}(\text{OH})_2 + \text{H}_2$
	Reaction with HCl	$\text{MCl}_2 + \text{H}_2$
	$\text{NaOH} + \text{H}_2\text{O}$	$\text{Na}_2[\text{Be}(\text{OH})_4] + \text{H}_2$ (Only Be reacts)
	Reaction with O_2	MO
	Reaction with H_2	MH_2
	Reaction with group 15 elements	$\text{M}_3\text{N}_2, \text{M}_2\text{P}_2$
	Reaction with group 16 elements	$\text{MS}_2, \text{MSe}, \text{MTe}$
	Reaction with halogens	MX_2
	Reaction with N_2	M_3N_2

❑ **Anomalous behaviour of beryllium :**

- Beryllium differs from the rest of the alkaline earth metals on account of its small atomic size, high electronegativity.
- It does not liberate H_2 from acids.
- It does not react with H_2O .
- It forms covalent compounds.
- BeO and $Be(OH)_2$ are amphoteric in nature.
- Be_3N_2 is volatile.
- It does not show coordination number of more than 4.

❑ **Diagonal relationship of Be with Al :**

- Oxides and hydroxides of both are amphoteric.
- Be_2C and Al_4C_3 react with water to produce methane.
- Be and Al both, do not impart colour to flame.
- Both become passive on treatment with conc. HNO_3 .
- $BeCl_2$ and $AlCl_3$ both are Lewis acids and are used as catalysts in Friedel Crafts reaction.

Industrial Uses of Some Important Compounds

Lime	Limestone	Plaster of Paris	Cement
<ul style="list-style-type: none"> – In the manufacture of bleaching powder, slaked lime and lime colours. – In the manufacture of cement, glass and mortar. – In the purification of sugar. – As basic lining in furnaces. 	<ul style="list-style-type: none"> – As flux in metallurgy of Fe – As a building material (marble) – In the manufacture of quick lime – In solvay process as a source of CO_2 and $Ca(OH)_2$ 	<ul style="list-style-type: none"> – For plastering walls – For making plaster casts – As industrial and sculptural material – For encasing limbs so that broken bones are set straight. 	As a building material

Biological Importance of Ca and Mg

Mg	Ca
Acts as cofactor for enzymes in phosphate transfer.	99% Ca of body is present in bones and teeth.
Present in chlorophyll.	Plays an important role in neuromuscular functions, cell membrane integrity and blood coagulation.

KEY POINT

- In alkaline earth metals, the formation of divalent cation lattice leads to evolution of energy due to strong lattice structure of divalent cations which easily compensates for the higher values of second ionisation energy of these metals.
- **Basic strength, Solubility and Thermal stability:**
 $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$
- **Solubility:** $BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$
 $BeSO_4 > MgSO_4 > CaSO_4 > \underbrace{SrSO_4 > BaSO_4}_{\text{Almost insoluble}}$
 $BeC_2O_4 > \underbrace{CaC_2O_4 < SrC_2O_4 < BaC_2O_4}_{\text{Sparingly soluble in water}}$
- **Stability:** $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$
 $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$

SELF CHECK

- Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy?
 (a) $BaSO_4$ (b) $SrSO_4$
 (c) $CaSO_4$ (d) $BeSO_4$ (JEE Main 2015)
- The metal that can not be obtained by electrolysis of an aqueous solution of its salt is
 (a) Cr (b) Ag
 (c) Ca (d) Cu (JEE Main 2014)
- Which of the following on thermal decomposition yields a basic as well as an acidic oxide?
 (a) $KClO_3$ (b) $CaCO_3$
 (c) NH_4NO_3 (d) $NaNO_3$ (AIEEE 2012)

p-BLOCK ELEMENTS (GROUP 13 AND 14)

- General Trends in Physical and Chemical Properties
- Anomalous Behaviour of the First Element
- Structure, Preparation, Properties and Uses of Some Important Compounds

TIPS TO REMEMBER

Group 13 Elements

- Group 13 of periodic table consists of following elements— ${}^5\text{B}$, ${}^{13}\text{Al}$, ${}^{31}\text{Ga}$, ${}^{49}\text{In}$ and ${}^{81}\text{Tl}$.

Physical properties :

Property	Trend
Atomic and ionic radii	Increase from B to Al then decrease from Al to Ga and then again increase
Ionisation enthalpy	Less than the corresponding members of alkaline earth metals and shows no regular trend down the group $\text{B} > \text{Tl} > \text{Ga} > \text{Al} > \text{In}$
Electronegativity	Decreases from B to Al and then increases
Metallic or electropositive character	First increases from B to Al and then decreases
Density	Increases down the group
Melting and boiling points	Melting points decrease sharply on moving down the group from B to Ga and then increase from Ga to Tl while boiling points decrease from B to Tl
Reducing character	$\text{Al} > \text{Ga} > \text{In} > \text{Tl}$
Physical state	All are solids, B is non-metallic, Al, Ga, In and Tl are silvery white metals.

Chemical properties :

Reaction	Specifications
$4\text{M} + 3\text{O}_2 \longrightarrow 2\text{M}_2\text{O}_3$	All react at high temperature, Tl forms some Tl_2O as well.
$2\text{Al} + \text{N}_2 \longrightarrow 2\text{AlN}$	Only Al reacts at high temperature

$2\text{M} + 3\text{X}_2 \longrightarrow 2\text{MX}_3$	All form trihalides, TlI_3 is unknown and $\text{Tl}^+[\text{I}_3]^-$ is formed.
$2\text{M} + 6\text{HCl} \longrightarrow 2\text{MCl}_3 + 3\text{H}_2$	All react with dilute mineral acids except B. Al rendered passive by HNO_3 particularly when concentrated.
$2\text{Al} + 2\text{NaOH} + 6\text{H}_2\text{O} \longrightarrow 2\text{NaAlO}_2 \cdot 2\text{H}_2\text{O} + 3\text{H}_2$	Only Al and Ga react.
$\text{M} + \text{NH}_3 \longrightarrow \text{MNH}_2$	All the metals form amides

KEY POINT

- Stability of +3 oxidation state:** $\text{B}^{3+} > \text{Al}^{3+} > \text{Ga}^{3+} > \text{In}^{3+} > \text{Tl}^{3+}$
- Stability of +1 oxidation state:** $\text{B}^+ < \text{Al}^+ < \text{Ga}^+ < \text{In}^+ < \text{Tl}^+$
- Lewis acid character:** $\text{BX}_3 > \text{AlX}_3 > \text{GaX}_3 > \text{InX}_3$ (where X is F, Cl, Br or I) and $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$
- Basic strength:** $\text{B}_2\text{O}_3 < \text{Al}_2\text{O}_3 < \text{Ga}_2\text{O}_3 < \text{In}_2\text{O}_3 < \text{Tl}_2\text{O}_3$
 $\text{B(OH)}_3 < \text{Al(OH)}_3 < \text{Ga(OH)}_3 < \text{In(OH)}_3 < \text{Tl(OH)}_3$

Anomalous behaviour of boron :

- Boron shows anomalous behaviour due to its small size, high nuclear charge, high electronegativity and non-availability of *d*-electrons.
- The main points of difference are as follows :
 - Boron is a typical non-metal whereas other members are metals.
 - It alone exhibits allotropy.
 - It is a bad conductor of electricity whereas others are good conductors.
 - It forms only covalent compounds whereas other elements also form some ionic compounds.
 - Hydroxides and oxides of boron are acidic in nature whereas those of others are amphoteric and basic.
 - The trihalides of boron (BX_3) exist as monomer whereas others exist as dimers.

CONCEPT MAP

GENERAL ORGANIC CHEMISTRY (ISOMERISM AND ELECTRON DISPLACEMENT EFFECTS)

The concept of isomerism illustrates the fundamental importance of molecular structure and shape in organic chemistry while the electron displacement through covalent bonds determines the polarity of molecules which helps to understand their physical and chemical properties.

ISOMERISM

The phenomenon of existence of two or more compounds having the same molecular formula but different chemical and physical properties is called isomerism.

Tautomerism

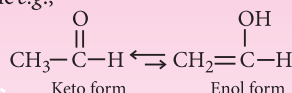
Compounds exist in dynamic equilibrium with each other.

- Arises due to migration of a hydrogen atom from one polyvalent atom to the other within the same molecule.

– In *dyad system*, H-atom oscillates between two polyvalent atoms linked together e.g.,

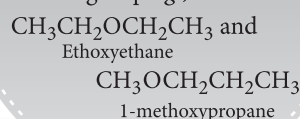


– In *triad system*, H-atom migrates from first polyvalent atom to third polyvalent atom within the same molecule e.g.,



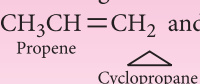
Metamerism

Compounds differ in the nature of alkyl groups attached on either side of the same functional group e.g.,



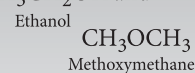
Ring Chain Isomerism

Compounds differ in the mode of linkage of C-atoms e.g., $\text{CH}_3\text{CH}=\text{CH}_2$ and



Functional Isomerism

Compounds differ in the nature of the functional group e.g., $\text{CH}_3\text{CH}_2\text{OH}$ and



Structural Isomerism

Arises when compounds have same molecular formula but different structures.

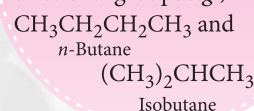
Chain or Nuclear Isomerism

Compounds differ in the nature of the carbon chain e.g., $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ and



Position Isomerism

Compounds differ in the position of multiple bond or functional groups e.g.,



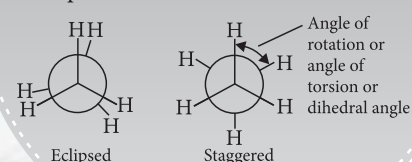
Optical Isomerism

Isomers differ only in behaviour towards the plane polarised light.

- Isomer which rotates the plane polarised light to the right is called *dextrorotatory*.
- Isomer which rotates the plane polarised light to the left is known as *laevorotatory*.

Conformational Isomerism

Isomers differ in relative arrangements of the atoms in space which result through rotation about a single bond e.g., staggered and eclipsed conformations of ethane.



Stereoisomerism

Arises when compounds have similar molecular formula and structural formula but differ in spatial arrangement of atoms or groups.

Inductive Effect

Displacement of σ -electrons along a saturated carbon chain whenever an atom of different electronegativity is present at the end of the chain is called inductive effect.

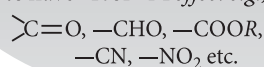
- The atom or group which has tendency to withdraw electrons towards itself is said to have *-I effect*.
- The atom or group which has tendency to repel electrons away from it is said to have *+I effect*.

Resonance or Mesomeric Effect

The flow of electrons from one part of the conjugated system to the other as a result of interaction between two π bonds or a π bond and lone pair of electrons.

- Groups which donate electrons to the double bond or to a conjugated system are said to have *+R* or *+M effect*. e.g., $-\text{OH}$, $-\text{OR}$, $-\text{SH}$, $-\text{SR}$, $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$ etc.

- Groups which withdraw electrons from a conjugated system towards themselves are said to have *-R* or *-M effect* e.g.,



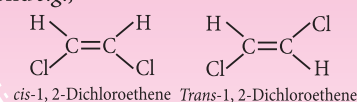
Electromeric Effect

Complete transfer of electrons of a multiple bond to one of the bonded atoms in presence of an attacking reagent is called electromeric effect.

- If the electrons are transferred towards the attacking reagent, the effect is called *+E effect*.
- If the electrons are transferred away from the attacking reagent, the effect is called *-E effect*.

Geometrical Isomerism

Isomers differ in the arrangement of atoms or groups in space due to hindered rotation around the double bond e.g.,



Hyperconjugation Effect

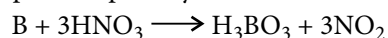
Delocalisation of σ electrons through overlapping of p -orbitals of a double bond with σ -orbital of the adjacent single bond is called hyperconjugation.

- The effect decreases with decrease in number of α -hydrogens i.e.,
 $-\text{CH}_3 > -\text{C}_2\text{H}_5 > (\text{CH}_3)_2\text{CH} > (\text{CH}_3)_3\text{C} -$

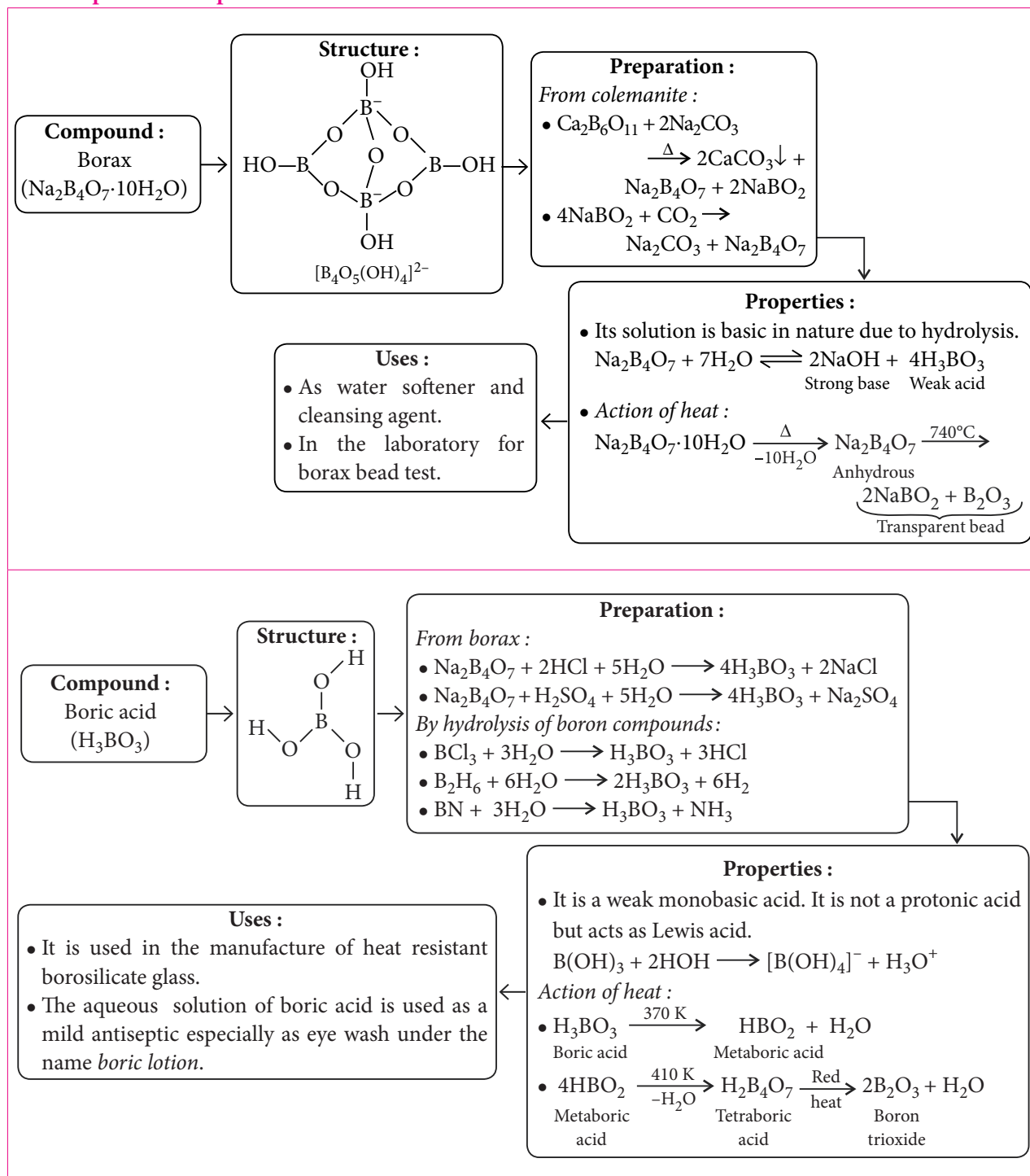
ELECTRON DISPLACEMENT EFFECTS

- Borates are more stable than aluminates.
- It exhibits maximum covalency of 4 while others exhibit a maximum covalency of 6.
- It does not decompose steam while other members do so.

- Concentrated nitric acid oxidises boron to boric acid while other elements become passive specially Al and Ga.



Some Important Compounds



Compound :
 AlCl_3

Structure :

Preparation :

- $2\text{Al} + 3\text{Cl}_2 \longrightarrow 2\text{AlCl}_3$
- $2\text{Al} + 6\text{HCl} \longrightarrow 2\text{AlCl}_3 + 3\text{H}_2$
- $\text{Al}_2\text{O}_3 + 3\text{C} + 3\text{Cl}_2 \xrightarrow{100^\circ\text{C}} 2\text{AlCl}_3 + 3\text{CO}$

Uses :

- Anhydrous AlCl_3 is used as a catalyst in Friedel-Crafts reaction and in cracking of petroleum.

Properties :

- Anhydrous AlCl_3 fumes in moist air due to hydrolysis and the resulting solution is acidic.
- $\text{AlCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_3 + 3\text{HCl}$
- $\text{AlCl}_3 + 3\text{NH}_4\text{OH} \longrightarrow \text{Al}(\text{OH})_3 \downarrow + 3\text{NH}_4\text{Cl}$
Gelatinous ppt.
(Insoluble in NH_4OH)
- $\text{AlCl}_3 + 3\text{NaOH} \longrightarrow \text{Al}(\text{OH})_3 \downarrow + 3\text{NaCl}$
(Soluble in excess NaOH)
- $\text{Al}(\text{OH})_3 + \text{NaOH} \longrightarrow \text{NaAlO}_2 + 2\text{H}_2\text{O}$
(Soluble metaaluminate)

❑ **Alums :** Alums are double sulphates of the type $\text{M}_2\text{SO}_4 \cdot \text{M}'_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ where M is a univalent cation like Na^+ , K^+ and NH_4^+ and M' is a trivalent cation like Al^{3+} , Fe^{3+} and Cr^{3+} .

Potash alum $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

Sodium alum $\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

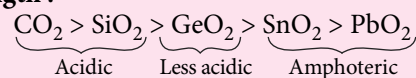
○ **Uses of alums:** Potash alum is used for purification of water, as styptic, in fire extinguishers, as mordant for dyeing and for tanning of leather.

❑ **Chemical properties :**

Group 14 Elements	Action of air	$\longrightarrow \text{MO}, \text{MO}_2$
	Reaction with H_2O	$\longrightarrow \text{SnO}_2 + \text{H}_2$
	Reaction with acids	$\longrightarrow \text{GeHCl}_3$ (with hot HCl gas); SnCl_2 and H_2PbCl_4 (with conc. HCl)
	Reaction with alkalis	$\longrightarrow \text{Na}_2\text{SiO}_3, \text{Na}_2\text{SnO}_3$
	Reaction with halogens	$\longrightarrow \text{MX}_4$ and MX_2

KEY POINT

- Pb does not decompose steam because of the protective layer of oxide.
- PbBr_4 and PbI_4 do not exist due to the fact that Pb^{4+} is a strong oxidising agent while Br^- and I^- ions are strongly reducing agents hence, Pb^{4+} cannot survive in presence of Br^- and I^- ion.
- Catenation tendency :** $\text{C} \gg \text{Si} > \text{Ge} \approx \text{Sn} \gg \text{P}$
- Acidic strength :**



❑ **Anomalous behaviour of carbon :**

- Carbon differs from rest of the members of group 14 because of its small size, high electronegativity, property of catenation and absence of d -orbitals.
- The main points of difference are as follows :
 - The melting and boiling points, ionisation energy and electronegativity of carbon are very high as compared to the rest of the members of the family.

Group 14 Elements

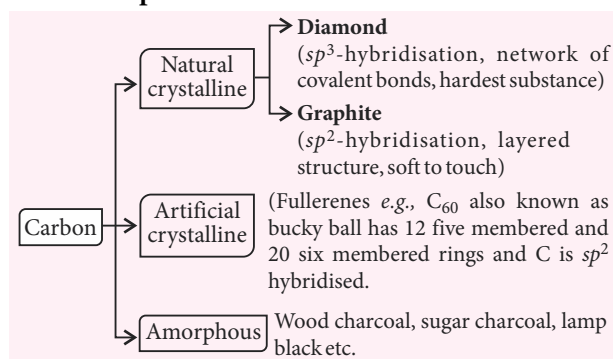
❑ Group 14 of periodic table consists of following elements ${}^6\text{C}$, ${}^{14}\text{Si}$, ${}^{32}\text{Ge}$, ${}^{50}\text{Sn}$ and ${}^{82}\text{Pb}$.

❑ **Physical properties :**

Atomic or covalent radii	$\text{C} < \text{Si} < \text{Ge} < \text{Sn} < \text{Pb}$
Ionisation energy	$\text{C} > \text{Si} > \text{Ge} > \text{Sn} > \text{Pb}$
Electronegativity	$\text{C} > \text{Si} \approx \text{Ge} \approx \text{Sn} < \text{Pb}$
Oxidation state	Stability of +4 oxidation state decreases down the group while that of +2 increases.
Melting and boiling points	Decrease from carbon to lead.
Density	Increases regularly from C to Pb
Allotropy	All elements show allotropy

- It has maximum tendency to show catenation as compared to other members of the family.
- It has high tendency to form $p\pi-p\pi$ multiple bonds while others form $p\pi-d\pi$ bonds and that also to a lesser extent.
- CO_2 is a gas while the dioxides of all other members are solids.

□ Allotropes of carbon :



□ Oxides of carbon :

Oxide	Preparation	Properties and uses
CO	<ul style="list-style-type: none"> • $2\text{C}_{(s)} + \text{O}_{2(g)} \xrightarrow{\Delta} 2\text{CO}_{(g)}$ • $\text{HCOOH} \xrightarrow[\text{conc. H}_2\text{SO}_4]{373 \text{ K}} \text{H}_2\text{O} + \text{CO}$ • $\text{C}_{(s)} + \text{H}_2\text{O}_{(g)} \xrightarrow{473-1273 \text{ K}} \underbrace{\text{CO}_{(g)} + \text{H}_{2(g)}}_{\text{Water gas}}$ • $2\text{C}_{(s)} + \text{O}_{2(g)} + 4\text{N}_{2(g)} \xrightarrow{1273 \text{ K}} \underbrace{2\text{CO}_{(g)} + 4\text{N}_{2(g)}}_{\text{Producer gas}}$ 	<ul style="list-style-type: none"> • It is a powerful reducing agent and reduces many metal oxides to the metal. • CO molecule acts as a donor and reacts with metals to form metal carbonyls. • It is an important fuel as it is a component of water gas, producer gas and coal gas. • It is toxic because it forms a complex with haemoglobin in the blood, and this complex is more stable than oxy-haemoglobin.
CO ₂	<ul style="list-style-type: none"> • $\text{C}_{(s)} + \text{O}_{2(g)} \xrightarrow{\Delta} \text{CO}_{2(g)}$ • $\text{CH}_{4(g)} + 2\text{O}_{2(g)} \xrightarrow{\Delta} \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(g)}$ • $\text{CaCO}_{3(s)} \xrightarrow{\Delta} \text{CaO}_{(s)} + \text{CO}_{2(g)}$ Limestone • $\text{CaCO}_{3(s)} + 2\text{HCl}_{(aq)} \longrightarrow \text{CaCl}_{2(aq)} + \text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)}$ 	<ul style="list-style-type: none"> • It is an acidic oxide, and reacts with bases forming salts. • Solid CO_2 is called 'dry ice' and is used to freeze foods and ice-cream. • It is not poisonous but in excess may lead to increase in greenhouse effect.

Some Important Compounds

□ SiO₂ :

- **Structure** : Silica has a three dimensional network structure in which each silicon is bonded to four oxygen atoms which are tetrahedrally disposed around silicon.
- **Uses** :
 - Sand is used in large amount to form mortar which is a building material.
 - Silica is used in the manufacture of glass and lenses for optical instruments.
 - Powdered quartz is used to manufacture silica bricks.
 - Silica gel ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$) is used in chromatography and also for adsorbing moisture.

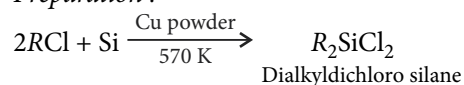
□ **Silicates** : The basic building unit of all silicates is tetrahedral SiO_4^{4-} ion. Depending upon the linkages of SiO_4^{4-} units, different types of structural arrangements are possible for silicates such as linear chains, cyclic chains, sheets, etc.

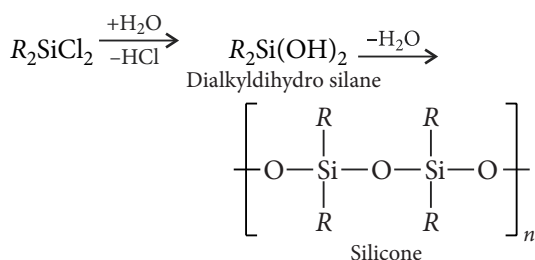
□ **Zeolites** : These are a class of three dimensional aluminosilicates. Their general formula is $M_{x/n}[\text{AlO}_2]_x[\text{SiO}_2]_y \cdot m\text{H}_2\text{O}$.

where, $M = \text{Na}^+, \text{K}^+ \text{ or } \text{Ca}^{2+}$, $n =$ charge on the simple cation, $m =$ no. of molecules of water of hydration.

□ **Silicones** : Silicones are polymeric organo-silicon compounds containing Si – O – Si linkages.

○ **Preparation** :





- **Uses :** They have good thermal oxidative stability. These are excellent water repellants and chemically inert substances. Liquid silicones are used as excellent lubricants.

SELF CHECK

13. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are
 (a) CH_3SiCl_3 and $Si(CH_3)_4$
 (b) $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$

- (c) $(CH_3)_2SiCl_2$ and CH_3SiCl_3
 (d) $SiCl_4$ and $(CH_3)_3SiCl$

(JEE Advanced 2015)

14. Which of the following exists as covalent crystals in the solid state?

- (a) Phosphorus (b) Iodine
 (c) Silicon (d) Sulphur

(JEE Main 2013)

15. Boron cannot form which one of the following anions?

- (a) BF_6^{3-} (b) BH_4^-
 (c) $B(OH)_4^-$ (d) BO_2^- (AIEEE 2011)

ANSWER KEYS (SELF CHECK)

1. (a) 2. (c) 3. (d) 4. (a) 5. (a)
 6. (b) 7. (c) 8. (b) 9. (c) 10. (d)
 11. (c) 12. (b) 13. (b) 14. (c) 15. (a)

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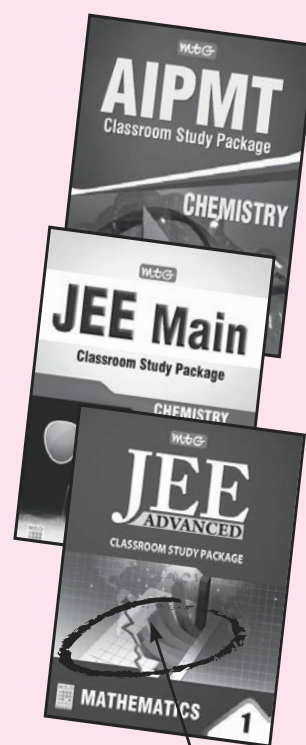
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QUESTIONS FOR PRACTICE

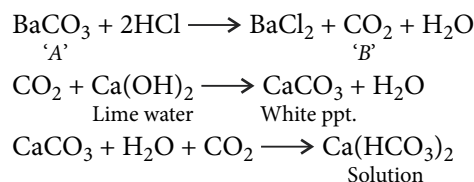
- First, second and third ionization energies are 737, 1451 and 7733 kJ mol⁻¹ respectively. The element can be
(a) Na (b) B (c) Al (d) Mg
- An element reacts with hydrogen to form a compound A, which on treatment of water liberates hydrogen gas. The element can be
(a) chlorine (b) selenium
(c) calcium (d) nitrogen.
- A white salt (A) evolves a colourless gas (B) with dilute HCl. Bubbling 'B' through lime water gives a precipitate 'C' which dissolves in excess of the gas. 'A' imparts apple green colour to the flame. Compound 'A' is
(a) CaCO₃ (b) BaCO₃
(c) Ca(OH)₂ (d) MgCO₃
- A sulphide ore is generally roasted to the oxide before reduction, because
(a) the enthalpy of formation of CO₂ is more than that of CS₂
(b) a metal sulphide is generally more stable than the metal oxide
(c) no reducing agent is found suitable for reducing a sulphide ore
(d) a sulphide ore cannot be reduced at all.
- In the metallurgy of zinc, the zinc dust obtained from roasting contains some zinc oxide. How is this removed?
(a) Smelting is employed.
(b) Shock coding with a shower of lead.
(c) Absorbance of UV light.
(d) X-ray method is used.
- The 1st IE of Li is 5.4 eV and the electron gain enthalpy of Cl is 3.6 eV. If the following reaction,
$$\text{Li}_{(g)} + \text{Cl}_{(g)} \longrightarrow \text{Li}^+ + \text{Cl}^-$$
is carried out at such a low pressure that resulting ions do not combine with each other, the ΔH of the reaction (in kcal mol⁻¹) is
(a) 118.8 (b) 124.52 (c) 83.0 (d) 41.508
- Which one out of the following statements is not correct for *ortho* and *para* hydrogen?
(a) They have different boiling point.
(b) *Ortho* form is more stable than *para* form.
(c) They differ in the spin of their protons.
(d) The ratio of *ortho* to *para* hydrogen increases with increase in temperature and finally pure *ortho* form is obtained.
- An alloy of Na + K is
(a) liquid at room temperature
(b) used in specially designed thermometers
(c) Both (a) and (b) (d) None of these.
- A white crystalline compound 'A' swells up on heating and gives violet coloured flame on bunsen flame. Its aqueous solution gives following reactions.
(I) It gives white ppt. with BaCl₂ in the presence of HCl.
(II) It gives white ppt. when treated with excess of NH₄OH. The ppt. dissolves in NaOH and reappears on boiling with conc. solution of NH₄Cl.
(III) It gives yellow ppt. with cobalt nitrite solution.
The compound 'A' is
(a) potash alum (b) borax
(c) diborane (d) aluminium sulphate.
- Carbon cannot be used in the reduction of Al₂O₃ because
(a) the enthalpy of formation of CO₂ is more than that of Al₂O₃
(b) pure carbon is not easily available
(c) the enthalpy of formation of Al₂O₃ is very high
(d) it is an expensive proposition.
- Identify the correct resonance structures of carbon dioxide from the ones given below :
(a) O—C≡O (b) $\bar{\text{O}}-\text{C}\equiv\text{O}$
(c) $\text{O}\equiv\text{C}-\text{O}^+$ (d) $\text{O}^--\text{C}\equiv\text{O}^+$
- Identify the statement that is not correct as far as structure of diborane is concerned.
(a) There are two bridging hydrogen atoms in diborane.
(b) Each boron atom forms four bonds in diborane.
(c) The hydrogen atoms are not in the same plane in diborane.
(d) All B—H bonds in diborane are similar.

13. Three elements A, B and C have the same number of protons in their nuclei but number of neutrons are different. Then, according to Mendeleev's periodic law, the positions of A, B and C in the periodic table will be
- in different group and different period
 - in same group but different period
 - in different group and same period
 - A, B and C will put together at a place.
14. 100 mL of tap water containing $\text{Ca}(\text{HCO}_3)_2$ was titrated with N/50 HCl with methyl orange as indicator. If 30 mL of HCl were required, the temporary hardness as parts of CaCO_3 per 10^6 parts of water.
- 150 ppm
 - 300 ppm
 - 450 ppm
 - 600 ppm
15. The chloride that can be extracted with ether
- NaCl
 - LiCl
 - BaCl_2
 - CaCl_2
16. Identify the statement that is not correct for Ellingham diagrams.
- These are the plots of $\Delta_f G^\circ$ vs T .
 - Each plot is a straight line unless phase change occurs.
 - These plots tell about the kinetics of reduction process.
 - These plots are based on thermodynamic concepts.
17. The soldiers of Napoleon army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White metallic tin buttons got converted to grey powder. This transformation is related to
- a change in the crystalline structure of tin
 - an interaction with nitrogen of the air at very low temperatures
 - a change in the partial pressure of oxygen in the air
 - an interaction with water vapour contained in the humid air.
18. Identify x , y , z for the following metallurgical process.
- Metal sulphide \xrightarrow{x} Metal oxide \xrightarrow{y} Impure metal \xrightarrow{z} Pure metal.
- x , y and z are respectively
- roasting, smelting, electrolysis
 - roasting, calcination, smelting
 - calcination, auto-reduction, bassemmerisation
 - none of the above is correct.
19. The electronic configuration of four elements are
 (I) $[\text{Xe}]6s^1$ (II) $[\text{Xe}]4f^{14}, 5d^1, 6s^2$
 (III) $[\text{Ar}]4s^2 4p^5$ (IV) $[\text{Ar}]3d^7, 4s^2$
 Select the incorrect statement about these elements.
- (I) is a strong reducing agent.
 - (II) is a d -block element.
 - (III) has high magnitude of $\Delta_{eg}H$.
 - (IV) exhibits variable oxidation states.
20. The strength of 5 volume H_2O_2 is
- 15
 - 1.5
 - 150
 - 0.15
21. An unknown inorganic compound (X) loses its water of crystallization on heating and its aqueous solution gives the following reactions.
- It gives a white turbidity with dilute HCl solution.
 - It decolourises a solution of iodine in potassium iodide.
 - It gives a white precipitate with silver nitrate solution which turns black on standing.
- Identify the compound (X).
- $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
 - $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$
 - $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
 - None of these
22. Refining of impure copper with zinc impurity is to be done by electrolysis using electrodes as
- | Cathode | Anode |
|-----------------|---------------|
| (a) pure copper | pure zinc |
| (b) pure zinc | pure copper |
| (c) pure copper | impure copper |
| (d) pure zinc | impure zinc |
23. The strongest oxidising agent among the given oxides is
- SiO_2
 - GeO_2
 - SnO_2
 - PbO_2
24. Select the incorrect statement.
- Sodium and potassium are 6th and 7th most abundant elements in the earth's crust.
 - When a pellet of NaOH is exposed to moist air, a liquid layer is formed around it, this is aqueous NaOH.
 - If a crystal of NaOH is exposed to air for longer periods it yields a white powder of Na_2CO_3 .
 - Lithium is one of the alkali metals and can be used in photoelectric cells.
25. Which of the following is incorrect order regarding the property indicated?
- $\text{Sc}^{3+} > \text{Cr}^{3+} > \text{Fe}^{3+} > \text{Mn}^{3+}$ -ionic radius
 - $\text{Sc} < \text{Ti} < \text{Cr} < \text{Mn}$ -density
 - $\text{Mn}^{2+} > \text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+}$ -ionic radius
 - $\text{FeO} < \text{CaO} > \text{MnO} > \text{CuO}$ -basic nature

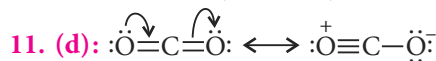
26. A molten ionic hydride on electrolysis gives
 (a) H^+ ions moving towards the cathode
 (b) H^+ ions moving towards the anode
 (c) H_2 which is liberated at anode
 (d) H_2 which is liberated at cathode.
27. The alkali metals form salt-like hydrides by the direct synthesis at elevated temperature. The thermal stability of these hydrides decreases in which of the following orders?
 (a) $NaH > LiH > KH > RbH > CsH$
 (b) $LiH > NaH > KH > RbH > CsH$
 (c) $CsH > RbH > KH > NaH < LiH$
 (d) $KH > NaH > LiH > CsH > RbH$
28. $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 \cdot 2H_2O$ or $Na[B(OH)_4]$
 How can this reaction be made to proceed in forward direction?
 (a) Addition of *cis*-1, 2 diol
 (b) Addition of borax
 (c) Addition of Na_2HPO_4
 (d) None of these
29. Consider the reactions,
 (I) $H_2O_2 + 2HI \longrightarrow I_2 + 2H_2O$
 (II) $HOCl + H_2O_2 \longrightarrow H_3O^+ + Cl^- + O_2$
 Which of the following statements is correct about H_2O_2 with reference to these reactions? Hydrogen peroxide is
 (a) an oxidising agent in both (I) and (II)
 (b) an oxidising agent in (I) and reducing agent in (II)
 (c) an reducing agent in (I) and oxidising agent in (II)
 (d) an reducing agent in both (I) and (II).
30. Pauling's electronegativity values for elements are useful in predicting
 (a) polarity of bonds in molecules
 (b) positions of elements in electromotive series
 (c) co-ordination number of elements
 (d) oxidation numbers of elements.

SOLUTIONS

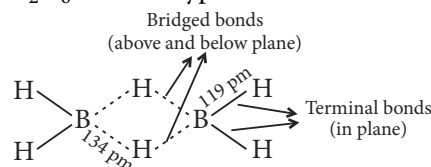
1. (d): Since IE_3 is much larger than IE_2 , the valence shell is expected to have two electrons. To remove a third electron, as measured by IE_3 , requires breaking into noble gas electronic configuration $2s^2 2p^6$.
2. (c): $Ca + H_2 \xrightarrow{2H_2O} Ca(OH)_2 + 2H_2$
 Thus the element is calcium.
3. (b): Since 'A' imparts apple green colour to the flame, it must contain Ba.



4. (a): The more stable CO_2 has higher enthalpy of formation than CS_2 .
5. (a): Smelting is done by using reducing agent.
6. (d): Given, $Li_{(g)} \longrightarrow Li^+_{(g)} + e^-$; $\Delta E_1 = 5.4 \text{ eV}$
 $Cl_{(g)} + e^- \longrightarrow Cl^-_{(g)}$; $\Delta E_2 = -3.6 \text{ eV}$
 $\Delta H = 5.4 - 3.6 = 1.8 \text{ eV} = 1.8 \times 23.06 \text{ kcal mol}^{-1}$
 $= 41.508 \text{ kcal mol}^{-1}$
7. (d): More than 75% *ortho* hydrogen in a sample can never be obtained.
8. (c): A characteristic feature of Na-K alloy.
9. (a): 'A' is potash alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
 It swells on heating due to evolution of water molecule and violet colour is due to potassium salt.
 (I) Sulphate ions combine with Ba^{2+} ion to form white ppt. of $BaSO_4$.
 (II) $Al_2(SO_4)_3 + 6NH_4OH \longrightarrow 2Al(OH)_3 + 3(NH_4)_2SO_4$
 ppt.
 $Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$
 Soluble
 $NaAlO_2 + NH_4Cl + H_2O \longrightarrow Al(OH)_3 + NaCl$
 ppt. + NH_3
 (III) $2K_2SO_4 + Na_4[Co(NO_2)_6] \longrightarrow K_4[Co(NO_2)_6] + 2Na_2SO_4$
 Yellow ppt.
10. (c): The enthalpy of formation of Al_2O_3 is very high and therefore, it cannot be reduced by carbon. It is reduced by electrolytic method.



12. (d): B_2H_6 has two types of B-H bonds



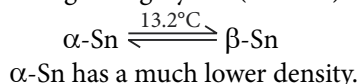
13. (d): Since, A, B and C are isotopes, thus, they will put at the same position in the Mendeleev's periodic table.
14. (a): 30 mL N/50 HCl \equiv 30 mL N/50 $Ca(HCO_3)_2$
 \equiv 30 mL N/50 $CaCO_3 \equiv$ 100 mL tap water.
 Mass of $CaCO_3$ in 100 mL tap water = $\frac{E \times N \times V}{1000}$

$$= \frac{50 \times 30}{50 \times 1000} = 0.03 \text{ g} \Rightarrow \text{hardness} = 300 \text{ ppm}$$

15. (b): LiCl is covalent in nature and thus soluble in weak polar organic solvents.

16. (c): Ellingham diagrams simply suggest whether the reduction process is feasible or not based on thermodynamic concepts but it cannot tell anything about kinetics of reaction.

17. (a): As temperature decreases, white tin (β -form) changes to grey tin (α -form).



18. (a): The conversion of metal sulphide to metal oxide involves the process of roasting.

The metal oxides can then be converted to impure metal by reduction process called smelting.

The conversion of impure metal to pure metal involves a process called electrolysis.

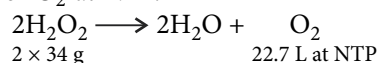
19. (b): (I) Since, the last electron enters in s -orbital, it is a s -block element and s -block elements are good reducing agents.

(II) Since, the last electron enters in f -block, it is a f -block element of $4f$ series.

(III) Electronic configuration reveals that it contains 7 electrons in its outer shell, so it is a halogen and halogens have high magnitude of $\Delta_{eg}H$.

(IV) The last electron enters in d -orbital, so it is a d -block element and shows variable oxidation states.

20. (a): 5 volume H_2O_2 solution means that 1 L of 5 volume H_2O_2 solution on decomposition produces 5 L of O_2 at NTP.



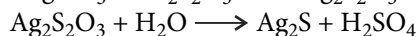
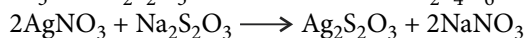
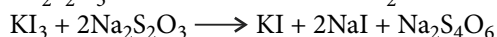
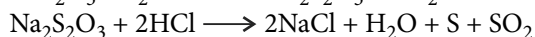
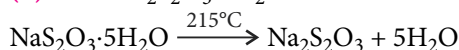
22.7 L O_2 at NTP will be obtained from $\text{H}_2\text{O}_2 = 68 \text{ g}$
 \therefore 5 L of O_2 at NTP will be obtained from H_2O_2

$$= \frac{68 \times 5}{22.7} \text{ g} = 14.98 = 15 \text{ g}$$

But 5 L of O_2 at NTP produced from 1 L of 5 volume H_2O_2

\therefore Strength of H_2O_2 solution = 15 g L^{-1}

21. (b): $X = \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$



22. (c): For purification, impure copper gets oxidised (deelectronation) falling into solution with mud, that's why impure copper at anode.

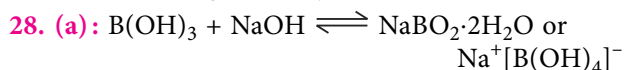
23. (d): For Pb the more stable oxidation state is +2 but in PbO_2 , it is in +4 oxidation state thus PbO_2 has great tendency to get reduced into PbO (+2 OS). Therefore, it acts as an oxidising agent.

24. (d): Lithium having the highest ionization energy amongst alkali metals cannot be used in photoelectric cells because it does not release electrons when exposed to light.

25. (a): Ionic radius (with same oxidation state) in the first transition series decreases across the period because effective nuclear charge per electron increases.

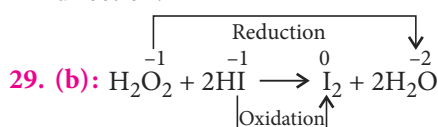
26. (c): Ionic hydride contains H^- ion. H^- ions undergo oxidation at anode and H_2 is liberated there.

27. (b): As the size of alkali metal ion increases, lattice energy decreases and hence the stability of the corresponding metal hydride decreases.

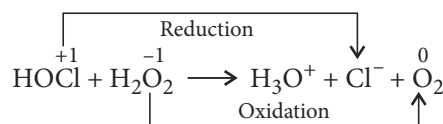


This reaction is reversible reaction because sodium metaborate formed in the reaction gets hydrolysed to regenerate B(OH)_3 and NaOH .

If some quantity of polyhydroxy compounds like *cis*-1,2-diol, catechol, glycerol etc. is added to the reaction mixture the metaborate ion combines with such polyhydroxy compounds to form chelated complex and the hydrolysis of BO_2^- ion is prevented which makes the reaction to proceed in forward direction.



H_2O_2 oxidises HI to I_2 hence, it behaves as oxidising agent.



Here, H_2O_2 reduces HOCl to Cl^- , thus, it acts as reducing agent.

30. (a): Pauling has estimated the approximate percentage of ionic character in various $A-B$ covalent bonds from the electronegativity difference of the two atoms forming the covalent bond.



ACE

YOUR WAY CBSE XII



Series 5

CHAPTERWISE PRACTICE PAPER : THE *d*-AND *f*-BLOCK ELEMENTS | COORDINATION COMPOUNDS

Time Allowed : 3 hours

Maximum Marks : 70

GENERAL INSTRUCTIONS

- All questions are compulsory.
- Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
- Q. no. 23 is a value based question and carries 4 marks.
- Q. no. 24 to 26 are long answer questions and carry 5 marks each.
- Use log tables if necessary, use of calculators is not allowed.

- Explain why Cu^{2+} ion is stable in aqueous solution.
- What is the type of isomerism shown by $[\text{Co}(\text{en})_3]\text{Cl}_3$?
- In which type of compounds transition metals show very low oxidation state?
- Why outer octahedral complexes are called high spin complexes?
- Ce(IV) is a good analytical reagent. Why?
- Write the IUPAC names of the following :
 - $[\text{CoCl}(\text{NO}_2)(\text{NH}_3)_4]\text{Cl}$
 - $[\text{PtCl}(\text{NH}_2\text{CH}_3)(\text{NH}_3)_2]\text{Cl}$
 - $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
- In the transition series, starting from lanthanum ($_{57}\text{La}$), the next element hafnium ($_{72}\text{Hf}$) has an atomic number of 72. Why do we observe this jump in atomic number?
- Discuss the nature of bonding in metal carbonyls.
- What is actinoid contraction? How is it different from lanthanoid contraction.
- Explain the structure of $[\text{NiCl}_4]^{2-}$ on the basis of V.B.T.
- The mercurous ion exists as Hg_2^{2+} ion while the cuprous ion exists as Cu^+ . Explain.
- The hexaaquamanganese (II) ion contains five unpaired electrons while the hexacyanomanganate ion contains only one unpaired electron. Explain using crystal field theory.
- Assign reasons for the following :
 - Actinoids exhibit greater range of oxidation states than lanthanoids.
 - Unlike Cr^{3+} , Mn^{2+} , Fe^{3+} and the subsequent other M^{2+} ions of the $3d$ series of element, the $4d$ and the $5d$ series metals generally do not form stable cationic species.
 - Transition metals generally form coloured compounds.
- Explain :
 - What will be the correct order for the wavelength of absorption in the visible region for the following : $[\text{Ni}(\text{NO}_2)_6]^{4-}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$?
 - $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green and becomes violet when ethane 1, 2-diamine is added to it.

15. (i) Why is Cr^{2+} reducing and Mn^{3+} oxidising in nature when both have d^4 configuration?
 (ii) Explain how $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ becomes purple coloured?

OR

- (i) Explain the following observations.
 (a) The metal-metal bonding is more frequent for the second and third series of transition elements than that for the first series.
 (b) The higher oxidation states are usually exhibited by members in the middle of a series of transition elements.
 (ii) Compare the nature of oxides of 3d-series of transition elements.
16. (i) A solution containing 0.319 g of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was passed through a cation exchange resin and the acid coming out of the resin required 28.5 mL of 0.125 M NaOH. Determine the correct structural formula of the complex. (Mol. wt. of the complex = 266.5 g mol^{-1})
 (ii) Write the chemical formula of Sodium (ethylenediaminetetraacetate) chromate(II).
17. Explain :
 (i) Why does melting point of transition elements generally increase towards the middle in each series?
 (ii) The enthalpies of atomisation of transition metals are quite high.
 (iii) Why is third ionisation energy of Mn exceptionally high?
18. (i) What do you mean by labile and non-labile complexes? Give examples.
 (ii) Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion?
19. Explain :
 (i) Chemistry of the actinoid elements is not so smooth as that of lanthanoids. Justify the statement by giving some examples from the oxidation state of these elements.
 (ii) Use Hund's rule to derive the electronic configuration of Ce^{3+} ion and calculate its magnetic moment on the basis of 'spin only' formula.

20. (i) Dilute equimolar solutions of each of the following compounds were prepared. Arrange these compounds in increasing order of molar conductivity of their solutions.

(a) $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ (b) $\text{K}[\text{Co}(\text{EDTA})]$
 (c) $[\text{Co}(\text{py})_3(\text{CN})_3]$ (d) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
 (e) $[\text{Pt}(\text{NH}_3)_6]\text{Br}_4$

- (ii) Out of the following two coordination entities, which is chiral (optically active)?

(a) *cis* - $[\text{CrCl}_2(\text{ox})_2]^{3-}$
 (b) *trans* - $[\text{CrCl}_2(\text{ox})_2]^{3-}$

21. Explain :

- (i) A yellow translucent solution is obtained on passing H_2S gas through an acidified solution of KMnO_4 . Identify the solution and write the balanced chemical equation.
 (ii) Describe the oxidising action of potassium dichromate and write the ionic equations for its reactions with
 (a) iodide ion (b) iron(II) solution and
 (c) H_2S .

22. Explain :

- (i) Among $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$, $[\text{Ni}(\text{Cl})_4]^{2-}$ and $[\text{CuCl}_4]^{2-}$ which
 (a) has square planar geometry?
 (b) remains colourless in aqueous solution and why?
 [Atomic number of Ag = 47, Ni = 28, Cu = 29]
 (ii) FeSO_4 solution mixed with $(\text{NH}_4)_2\text{SO}_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} ion but CuSO_4 solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of Cu^{2+} ion. Explain why?

23. Dr. S.P. Rahman, a professor of Medical Science, organised a seminar on cancer. The following paragraph highlights the important message given by him :

"Cancer is not a communicable disease and it occurs due to unlimited growth of body cells leading to tumours. We should shake hands, eat together with the people suffering from cancer. These activities will boost up the confidence in them for living."

- (i) Mention the values reflected by the message given by Dr. Rahman.
 (ii) Write the name of coordination compound used for the treatment of cancer and give its structure.
 (iii) Give the uses of two other coordination compounds in medicinal chemistry.

24. (i) What happens when : (give only ionic equations)
- potassium manganate is treated with ozone.
 - sodium thiosulphate is treated with acidified $K_2Cr_2O_7$.
 - potassium iodide is treated with alkaline $KMnO_4$.
- (ii) Give reasons for the following :
- The transition metals form interstitial compounds.
 - Silver halides find use in photography.

OR

- (i) What happens when : (give only ionic equations)
- hydrogen peroxide is treated with acidified potassium dichromate solution.
 - hydrogen peroxide is treated with acidified potassium permanganate solution.
- (ii) Mention the direct consequence of the following factors on the chemical behaviour of the transition elements.
- They have incompletely filled d -orbitals in the ground state or in one of the oxidised states of their atoms.
 - They contribute more valence electrons per atom in the formation of metallic bonds.
25. For the complex $[Fe(en)_2Cl_2]Cl$, identify :
- oxidation number of iron and name of complex (At. no. of Fe = 26)
 - the hybrid orbitals and shape of the complex
 - the magnetic behaviour of the complex
 - the number of geometrical isomers and
 - whether there is any optical isomer also.

OR

- (i) Describe the application of complex formation in qualitative identification of cations. Give specific examples.
- (ii) (a) Draw the structure of the $[Pt(trien)]^{2+}$ chelate.
 (b) How many bonding sites are present in this ligand?
 (c) What is the chemical name of this ligand?
26. The gas liberated, on heating a mixture of two salts with NaOH, gives a reddish-brown precipitate with an alkaline solution of K_2HgI_4 . The aqueous solution of the mixture on treatment with $BaCl_2$ gives a white precipitate, which is sparingly soluble

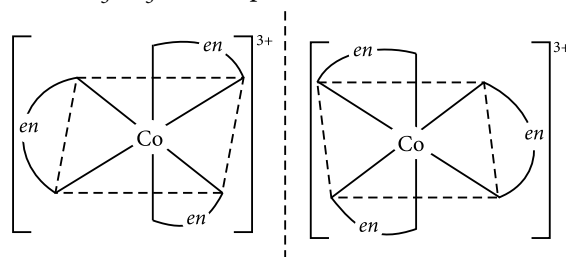
in conc. HCl. On heating the mixture with $K_2Cr_2O_7$ and conc. H_2SO_4 , red vapours (A) are produced. The aqueous solution of the mixture gives a deep blue colouration (B) with potassium ferricyanide solution. Identify the radicals in the given mixture and write the balanced equations for the formation of (A) and (B).

OR

A green chromium compound (A) on fusion with alkali gives a yellow compound (B) which on acidification gives an orange coloured compound (C). (C) on treatment with NH_4Cl gives an orange coloured product (D) which on heating decomposes to give back compound (A). Identify (A), (B), (C) and (D) and write down the structure of (C).

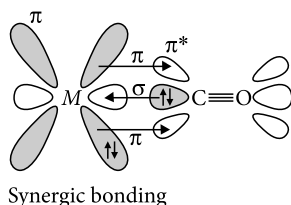
SOLUTIONS

- Hydration enthalpy of Cu^{2+} ion is more negative which more than compensates for the high second ionisation enthalpy of Cu.
- $[Co(en)_3]Cl_3$ shows optical isomerism.

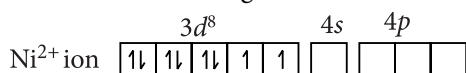


- Transition metals show very low oxidation states in compounds having ligands which act as π acceptors e.g., CO, NO etc.
- No pairing occurs in outer octahedral complexes, hence, they have many unpaired electrons and show large values of magnetic moments.
- The E° value for Ce^{4+}/Ce^{3+} is 1.74 V which suggests that it can oxidise water however, the reaction rate is very slow and hence Ce (IV) is a good analytical reagent.
- (i) Tetraamminechloridonitrito-N-cobalt (III) chloride.
 (ii) Diamminechlorido(methylamine)platinum (II) chloride
 (iii) Hexaaquamanganese (II) ion
 (iv) Hexaaquatitanium (III) ion

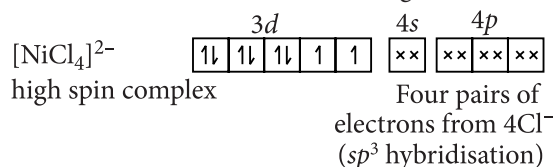
7. This is because after $_{57}\text{La}$, filling of $4f$ -orbital starts which is complete at atomic number 71. These 14 elements therefore, belong to f -block and are placed separately at the bottom of the periodic table.
8. The metal-carbon bond in metal carbonyls possess both σ and π character. The $M\text{-C}$ σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The $M\text{-C}$ π -bond is formed by the donation of a pair of electrons from a filled d -orbital of metal into the vacant antibonding π^* -orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.



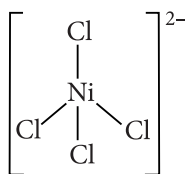
9. The gradual decrease in the atomic as well as ionic sizes (M^{3+} ions) of actinoids along the series is called actinoid contraction. It is different from the lanthanoid contraction by the fact that the decrease in size or contraction between two successive elements is higher in actinoids due to poor screening by $5f$ -electrons.
10. In $[\text{NiCl}_4]^{2-}$, Ni is in +2 oxidation state and has $3d^8$ outer electronic configuration.



Under the influence of weak field ligand :

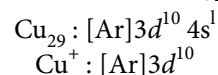


It is sp^3 hybridised hence, structure is tetrahedral.



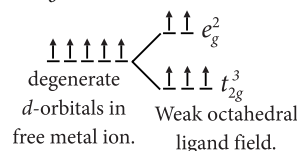
11. $\text{Hg}_{80} : [\text{Xe}]_{54} 4f^{14} 5d^{10} 6s^2$
 $\text{Hg}^+ : [\text{Xe}]_{54} 4f^{14} 5d^{10} 6s^1$

In Hg(I) , there is one unpaired electron and we expect Hg(I) (mercurous) salts to be paramagnetic. But mercurous salts are found to be diamagnetic which is only possible when $6s$ orbitals of the two Hg^+ ions overlap to form a $\text{Hg}-\text{Hg}$ covalent bond. Hence, mercurous ion exists as Hg_2^{2+} .



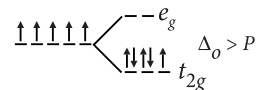
Cu(I) has no unpaired electron to form dimeric species and also its salts are diamagnetic hence, it exists as Cu^+ .

12. $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ contains $\text{Mn}^{2+} - 3d^5$ configuration
 C.N. = 6, octahedral structure, H_2O is a weak field ligand, hence $\Delta_o < P$



Electrons enter into e_g orbital before pairing. It has five unpaired electrons.

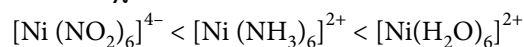
$[\text{Mn}(\text{CN})_6]^{4-}$ contains Mn^{2+} ion- $3d^5$ configuration. C.N. = 6, octahedral geometry, CN^- is strong field ligand, $\Delta_o > P$



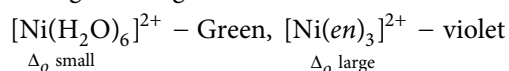
Hence pairing of electrons in t_{2g} orbitals takes place. It has only one unpaired electron.

13. (i) This is because there is less energy difference between $5f$ and $6d$ orbitals in actinoids than the energy difference between $4f$ and $5d$ orbitals in case of lanthanoids.
- (ii) This is because due to lanthanoid contraction the expected increase in size does not occur hence, they have very high value of ionisation enthalpy.
- (iii) This is due to $d-d$ transition. When visible (white) light falls on transition metal compounds, they absorb certain radiation of visible light for transition of electrons from lower d level to higher d level and transmit the remaining ones. The colour observed corresponds to complementary colour of the light absorbed.
14. (i) The strength of the ligands in the spectrochemical series follows the order (increasing Δ_o value) $\text{H}_2\text{O} < \text{NH}_3 < \text{NO}_2^-$

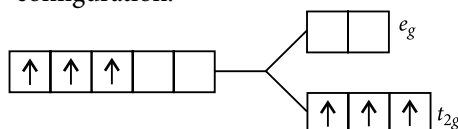
As $\Delta_o = \frac{hc}{\lambda}$, the order of wavelength absorbed is



- (ii) Ethane-1,2-diamine is stronger ligand than H_2O . When H_2O molecule is replaced by ethane-1,2-diamine (*en*), the crystal field splitting energy (Δ_o) increases. Complex absorbs light of higher frequency for $d-d$ transition and hence colour of the complex changes from green to violet.



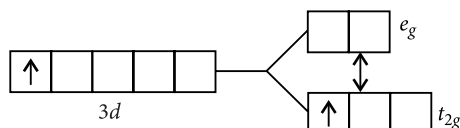
15. (i) Cr^{2+} is reducing as its configuration changes from d^4 to d^3 , a more stable half filled t_{2g} configuration.



Mn^{3+} is oxidising because its configuration also changes from d^4 to d^5 (which is half-filled) and has extra-stability.

- (ii) In $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, titanium has $3d^1 4s^0$ configuration. In Ti^{3+} ion, the d -orbitals split up into two parts t_{2g} and e_g . The t_{2g} part has three out of five d -orbitals (d_{xy} , d_{yz} , d_{zx}) with energy lower than the atomic orbitals whereas e_g have two orbitals ($d_{x^2-y^2}$ and d_{z^2}) having energy more than the atomic orbitals.

Due to less energy difference between t_{2g} and e_g orbitals, the electrons transit between these two orbital groups (called $d-d$ transition). The energy required for this purpose is sufficiently available in the visible region. The $d-d$ transition absorbs yellow region light and therefore colour observed is purple (complementary colour).



OR

- (i) (a) Nearly all the transition metals have the simple *hcp*, *ccp* or *bcc* lattice characteristics of true metals in which atoms are held together by strong metal-metal bonding. As we go down the

group, electrons of elements of second and third series are available more easily as compared to first series hence, metal-metal bonding is more frequent in $4d$ and $5d$ -series of elements.

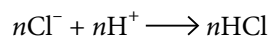
- (b) The lesser number of oxidation states on the extreme ends of the series can be due to the presence of too few electrons or due to the presence of too many electrons and thus, fewer empty orbitals to share electrons with the ligands. In the middle of the series, ns and $(n-1)d$ electrons are involved hence, higher oxidation states are exhibited by them.

- (ii) While moving along a period from Sc to Zn, basic nature decreases and acidic nature increases.

Also, with increase in the oxidation state of a given transition metal, the covalent character of its compound increases and thus acidic character also increases.

16. (i) Let the number of Cl^- ion outside the coordination sphere, i.e., the number of ionisable Cl^- ions be n .

When the solution of the complex is passed through cation exchanger, $n\text{Cl}^-$ ions will combine with $n\text{H}^+$ ions to form $n\text{HCl}$.



$$\therefore 1 \text{ mole of complex} = n \text{ moles of HCl} \\ \equiv n \text{ moles of NaOH.}$$

$$\text{Moles of the complex} = \frac{0.319}{266.5} = 0.0012 \text{ mol}$$

$$\text{Moles of NaOH used} = \frac{28.5 \times 0.125}{1000} = 0.0036 \text{ mol}$$

Thus, $0.0012 \text{ mol of complex} \equiv 0.0036 \text{ mol of NaOH} \equiv 0.0036 \text{ mol of HCl}$

$$\therefore 1 \text{ mole of complex} = \frac{0.0036}{0.0012} = 3 \text{ mol of HCl}$$

$$\therefore n = 3$$

Thus, all the Cl^- ions are outside the coordination sphere and formula of the complex is $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$.

- (ii) $\text{Na}_2[\text{Cr}(\text{EDTA})]$

17. (i) The transition elements are characterised by high melting points. It is attributed to the involvement of greater number of electrons from $(n-1)d$ orbital in addition to ns electrons

in the interatomic metallic bonding. In general, greater the number of valence electrons, stronger is the resultant metallic bonding. In any series, the melting point rises to a maximum at about the middle of each series which indicates that one unpaired electron per d -orbital is particularly favourable for strong interatomic bonding.

(ii) The enthalpy of atomisation is the amount of energy (heat) required to break the metal lattice to get free atoms. As transition metals contain a large number of unpaired electrons, they have strong interatomic attractive forces, *i.e.*, metallic bonds. As a large amount of energy is required to break these metallic bonds, transition metals have high enthalpies of atomisation.

(iii) Mn^{2+} has the outer electronic configuration $[\text{Ar}]3d^5$. Due to highly symmetrical, half-filled d -subshell, the removal of third electron is very difficult. Therefore, third ionisation energy of Mn is very high.

18. (i) Complex ions in which ligands can be interchanged rapidly are said to be labile. $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ are labile complexes.

A complex ion that exchanges ligands slowly is said to be non-labile or inert. In general, complex ions of the first transition series, except for those of Cr(III) and Co(III) are kinetically labile. Those of the second and third transition series are generally kinetically inert.

(ii) Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are same with respect to each other.

19. (i) Lanthanoids show only few oxidation states such as +2, +3 and +4 (+3 oxidation state is the most stable one). Actinoids show more oxidation states (from +3 to +6), +3 being the most stable. Lesser number of oxidation states for lanthanoids is due to large energy gap between $4f$, $5d$ and $6s$ orbitals whereas the energy gap between $5f$, $6d$ and $7s$ orbitals is comparatively small. Hence actinoids show more oxidation states.

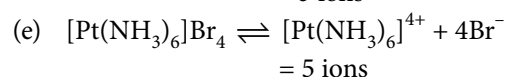
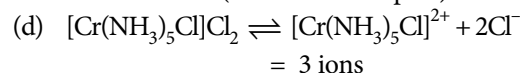
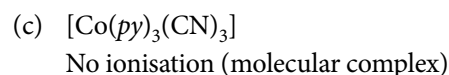
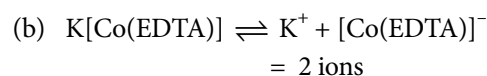
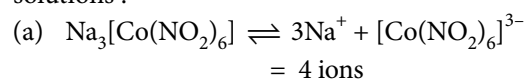
(ii) $\text{Ce}(58) : [\text{Xe}] 4f^1 5d^1 6s^2$ (1)
 $\text{Ce}^{3+} : [\text{Xe}] 4f^1$

$\Rightarrow n = 1$ (only one unpaired electron)

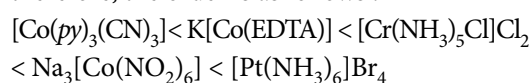
By 'spin-only' formula,

$$\begin{aligned}\text{Magnetic moment of } \text{Ce}^{3+} (\mu) &= \sqrt{n(n+2)} \\ &= \sqrt{1(1+2)} = \sqrt{3} \\ &= 1.73 \text{ BM}\end{aligned}$$

20. (i) These compounds will ionise as follows in their solutions :



As molar conductivity is proportional to the number of ions produced in the solution, therefore, the order is as follows :

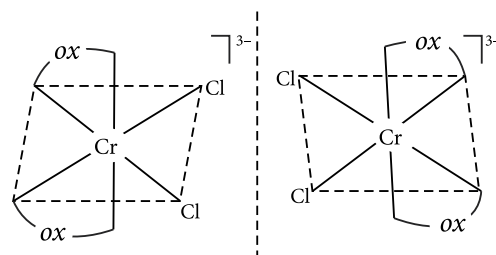


(ii) (a) $\text{cis}-[\text{CrCl}_2(\text{ox})_2]^{3-}$

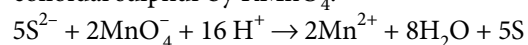
(b) $\text{trans}-[\text{CrCl}_2(\text{ox})_2]^{3-}$

Out of the two, (a) $\text{cis}-[\text{CrCl}_2(\text{ox})_2]^{3-}$ is chiral (optically active).

The two entities are represented as



21. (i) When H_2S gas is passed through an acidified solution of KMnO_4 , a translucent solution is obtained due to the oxidation of H_2S into colloidal sulphur by KMnO_4 .



The yellow translucent solution is of colloidal sulphur in water.

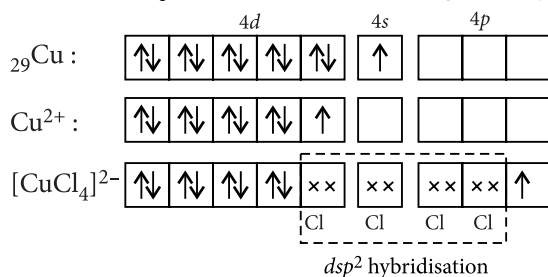
(ii) $\text{K}_2\text{Cr}_2\text{O}_7$ acts as a powerful oxidising agent in acidic medium (dilute H_2SO_4). the $\text{Cr}_2\text{O}_7^{2-}$ ion takes up electrons and hence acts as oxidising agent. In this reaction, Cr (+6) is reduced to Cr (+3). The potential equation for reduction is $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ ($E^\circ = 1.33 \text{ V}$)

(a) Iodine is liberated from iodide solution.
 $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{I}^- \rightarrow 2\text{Cr}^{3+} + 3\text{I}_2 + 7\text{H}_2\text{O}$

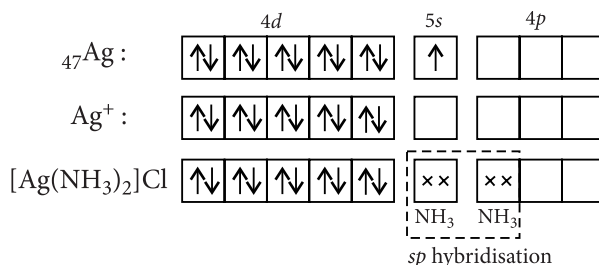
(b) Ferrous ion is oxidised to ferric ion.
 $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$

(c) H_2S is oxidised to sulphur.
 $\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 3\text{H}_2\text{S} \rightarrow 2\text{Cr}^{3+} + 3\text{S} + 7\text{H}_2\text{O}$

22. (i) (a) $[\text{CuCl}_4]^{2-}$ has the square planar geometry.



(b) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ is colourless because there are no unpaired electrons in its d -orbitals hence, no $d-d$ transition is possible.



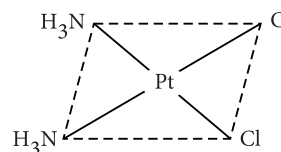
(ii) On mixing FeSO_4 and $(\text{NH}_4)_2\text{SO}_4$ in 1:1 molar ratio, a double salt, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (Mohr's salt) is formed which on ionisation gives all constituent ions. Thus, it gives the test of Fe^{2+} ions.

When CuSO_4 solution and aqueous ammonia are mixed in 1 : 4 molar ratio, a complex salt, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ is formed. This complex compound on ionisation gives $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and SO_4^{2-} ions and not Cu^{2+} ions. Due to absence of free Cu^{2+} ions, it does not give the test of Cu^{2+} ions.

23. (i) We should show compassion and empathy towards cancer patients and they should be encouraged to live a normal life.

(ii) *cis*-platin, *cis* $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is used for the treatment of cancer.

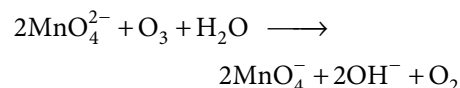
It has a square planar structure.



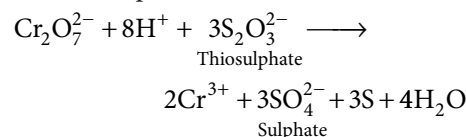
(iii) (a) Copper and iron when present in toxic proportions in plants and animals are removed by chelating agent *D*-penicillamine and desferrioxime -B.

(b) EDTA is used for the treatment of lead poisoning.

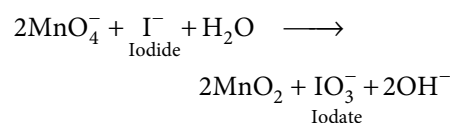
24. (i) (a) Potassium permanganate is formed.



(b) Sodium sulphate is formed



(c) Potassium iodate is formed



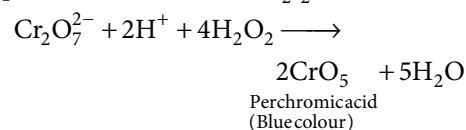
(ii) (a) Transition metals form a large number of interstitial compounds because small atoms of certain non metallic elements (H, B, C, N, etc.) get trapped in voids or vacant spaces of lattice of the transition metals.

As a result of filling up of the interstitial spaces such interstitial compounds are hard and rigid.

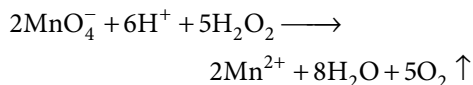
(b) Under the action of light, decomposition of silver bromide takes place in traces where it is illuminated. The number of silver atoms formed is proportional to the quantity of light falling on the surface.

OR

(i) (a) A deep blue colour, due to the formation of perchromic acid $[\text{CrO}(\text{O}_2)_2]$, is obtained.

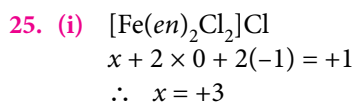


(b) Oxygen is evolved.



(ii) (a) Vacant d -orbitals can accept lone pair of electrons donated by other groups (ligands), consequently transition elements form a large number of complex compounds. Paramagnetism and colour of compound is also due to incompletely filled d -orbital.

(b) Due to presence of large number of valence electrons per atom, the metallic bonds in transition elements are quite strong. Due to the presence of strong metallic bonds the transition metals are hard, possess high densities and high enthalpies of atomisation.



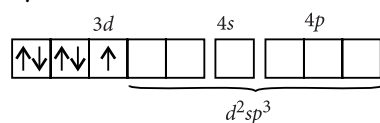
\therefore Fe is present as Fe (III).

Name of the complex is :
 dichloridobis(ethane-1, 2-diamine)iron (III) chloride

(ii) Coordination number of Fe is 6 therefore, hybridisation is as follows :



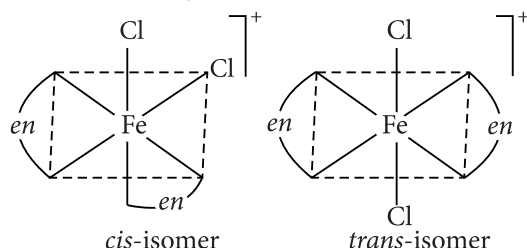
en ligand is a strong field ligand and therefore, electrons get paired up giving d^2sp^3 hybridisation.



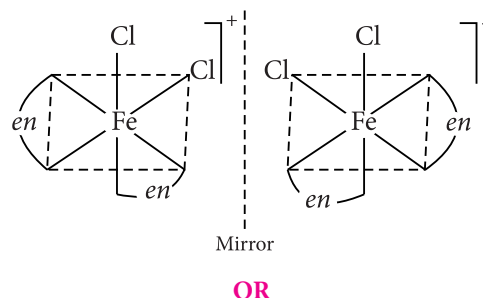
Shape of the complex : Octahedral

(iii) As it has one unpaired electron, it is paramagnetic.

(iv) It shows two geometrical isomers.

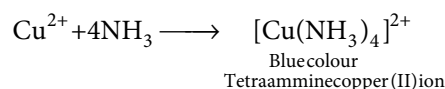


(v) The *cis*-isomer will show optical isomerism.

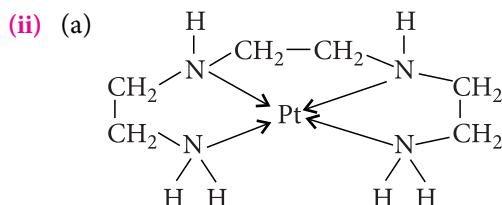
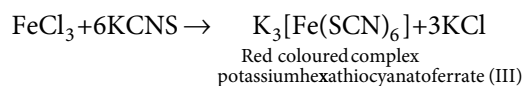


(i) Complex formation is frequently encountered in qualitative identification of cations. For example,

(a) Identification of Cu^{2+} ion is based on the formation of blue coloured tetraamminecopper (II) ion in solution.



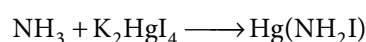
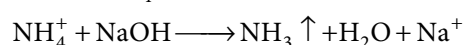
(b) Fe^{3+} ion can be identified by the blood red coloured complex, potassium hexathiocyanoferrate (III), it forms with KCNS.



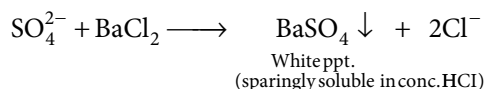
(b) The ligand present in above chelate is tetradentate *i.e.*, it has four bonding sites.

(c) The chemical name of the ligand is
 N, N-bis(2-aminoethyl)-1,2-ethanediamine.

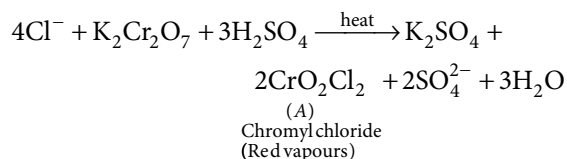
26. Liberation of gas (might be NH_3) with NaOH and reddish brown precipitate (which are due to liberated NH_3 and K_2HgI_4) with Nessler's reagent (K_2HgI_4) confirms the presence of ammonium radical (NH_4^+).



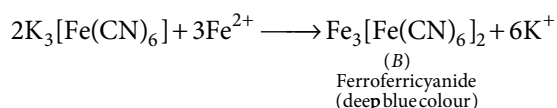
Formation of white precipitate with BaCl_2 , which is sparingly soluble in conc. HCl , indicates the presence of sulphate radical (SO_4^{2-}).



Evolution of red vapours (CrO_2Cl_2) with $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 confirms the presence of chloride radical (Cl^-).



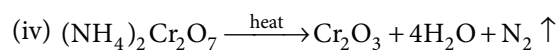
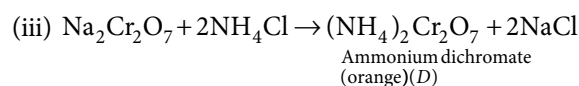
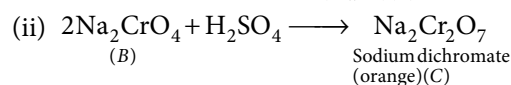
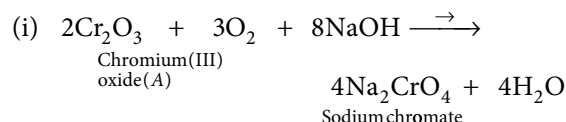
Formation of deep blue colouration (B) with potassium ferricyanide solution confirms the presence of ferrous radical (Fe^{2+}).



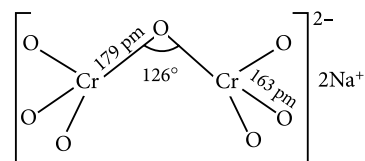
Hence in the mixture, NH_4^+ , Fe^{2+} , Cl^- and SO_4^{2-} radicals are present and (A) is chromyl chloride (CrO_2Cl_2) and (B) is ferroferricyanide, $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$.

OR

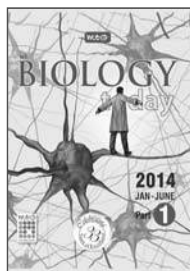
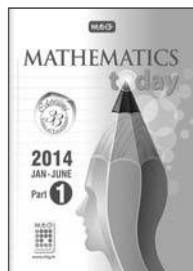
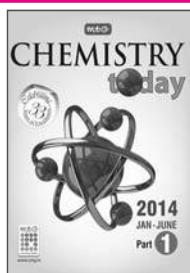
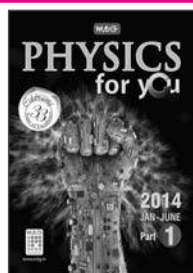
The yellow coloured compound (B) is sodium chromate which is formed on fusion of chromium (III) oxide (A) and NaOH . Compound (B) on acidification gives sodium dichromate (C), which on treatment with NH_4Cl gives ammonium dichromate (D), which on heating gives chromium (III) oxide.



Structure of (C) :



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EXAMINER'S MIND

CLASS XII



The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII. This year JEE (Main & Advanced)/AIPMT/AIIMS/other PMTs have drawn their papers heavily from NCERT books.

THE *p*-BLOCK ELEMENTS | THE *d*- AND *f*-BLOCK ELEMENTS

SECTION - I

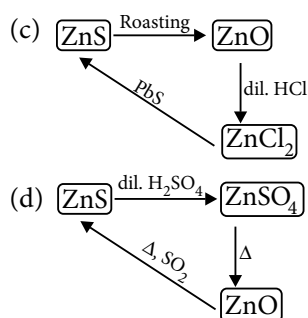
Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- The correct order for decreasing acidic strength of oxoacids of gp. 15 is
 (a) $\text{HNO}_3 > \text{H}_3\text{SbO}_4 > \text{H}_3\text{AsO}_4 > \text{H}_3\text{PO}_4$
 (b) $\text{H}_3\text{PO}_4 > \text{H}_3\text{AsO}_4 > \text{H}_3\text{SbO}_4 > \text{HNO}_3$
 (c) $\text{HNO}_3 > \text{H}_3\text{PO}_4 > \text{H}_3\text{AsO}_4 > \text{H}_3\text{SbO}_4$
 (d) $\text{HNO}_3 > \text{H}_3\text{AsO}_4 > \text{H}_3\text{PO}_4 > \text{H}_3\text{SbO}_4$
- Consider the following reaction :

$$x\text{MnO}_4^- + y\text{C}_2\text{O}_4^{2-} + z\text{H}^+ \rightarrow x\text{Mn}^{2+} + 2y\text{CO}_2 + \frac{z}{2}\text{H}_2\text{O}$$

 The values of x , y and z in the reaction are respectively
 (a) 2, 5 and 16 (b) 5, 2 and 16
 (c) 5, 2 and 8 (d) 2, 5 and 18.
- Which of the following is the wrong statement?
 (a) Ozone is violet-black in solid state.
 (b) Ozone is a diamagnetic gas.
 (c) NOCl and ONO^- are not isoelectronic.
 (d) O_3 molecule is bent.
- Bromine vapours will turn moist starch iodide paper
 (a) brown (b) red
 (c) violet (d) colourless.
- If the lanthanoid element with x *f*-electrons has a pink colour, then the lanthanoid with $(14 - x)$ *f*-electrons will have the colour as
 (a) blue (b) red (c) green (d) pink.
- Which noble gas does not form clathrates
 (a) Xe (b) Kr (c) He (d) Ar
- Which one of the following elements has the highest tendency towards catenation ?
 (a) Oxygen (b) Selenium
 (c) Sulphur (d) Tellurium
- CrO_3 dissolves in aqueous NaOH to give
 (a) CrO_4^{2-} (b) $\text{Cr}(\text{OH})_3$
 (c) $\text{Cr}_2\text{O}_7^{2-}$ (d) $\text{Cr}(\text{OH})_2$
- Solution of HgCl_2 when reacts with PH_3 gas, produces
 (a) PH_4Cl (b) Hg
 (c) Hg_3P_2 (d) PCl_3
- The order of the $\text{X}-\text{O}-\text{X}$ bond angles is
 (a) $\text{F}_2\text{O} > \text{Cl}_2\text{O} > \text{Br}_2\text{O}$
 (b) $\text{F}_2\text{O} < \text{Cl}_2\text{O} < \text{Br}_2\text{O}$
 (c) $\text{Cl}_2\text{O} > \text{F}_2\text{O} > \text{Br}_2\text{O}$
 (d) none of these.
- Hydrolysis of one mole of peroxodisulphuric acid produces
 (a) two moles of sulphuric acid
 (b) two moles of peroxomonosulphuric acid
 (c) one mole of sulphuric acid and one mole of peroxomonosulphuric acid
 (d) one mole of sulphuric acid, one mole of peroxomonosulphuric acid and one mole of hydrogen peroxide.
- The shape of ClO_3^- ion is
 (a) pyramidal (b) tetrahedral
 (c) triangular planar (d) triangular bi-pyramidal.
- Which diagram shows correct set of reactions for ZnS ?
 (a)
$$\begin{array}{ccc} \boxed{\text{ZnS}} & \xrightarrow{\text{dil. HCl}} & \boxed{\text{ZnCl}_2} \\ & \swarrow \text{H}_2\text{S/H}^+ & \downarrow \text{H}_2\text{SO}_4 \\ & & \boxed{\text{ZnSO}_4} \end{array}$$
 (b)
$$\begin{array}{ccc} \boxed{\text{ZnS}} & \xrightarrow{\text{Roasting}} & \boxed{\text{ZnO}} \\ & \swarrow \text{NH}_4\text{Cl} + \text{NH}_4\text{OH} & \downarrow \text{dil. H}_2\text{SO}_4 \\ & & \boxed{\text{ZnSO}_4} \end{array}$$



14. What are the products obtained when ammonia is reacted with excess of chlorine?
 (a) N_2 and NCl_3 (b) N_2 and HCl
 (c) N_2 and NH_4Cl (d) NCl_3 and HCl
15. If X is a member of chalcogen family, the highest stability of X^{2-} is exhibited by
 (a) oxygen (b) selenium
 (c) tellurium (d) sulphur.
16. Which one of the following is a diamagnetic ion ?
 (a) Co^{2+} (b) Cu^{2+} (c) Mn^{2+} (d) Sc^{3+}
17. Which of the following is used as a good oxidising agent in analytical chemistry ?
 (a) Gd (III) (b) Ce(IV)
 (c) Eu(II) (d) Lu(III)
18. Among the following oxides, the least acidic is
 (a) P_4O_6 (b) P_4O_{10}
 (c) As_4O_6 (d) As_4O_{10}
19. Hydrolysis of one mole of which of the following requires maximum volume of 1 M NaOH for complete neutralisation and maximum volume of 0.1M $\text{K}_2\text{Cr}_2\text{O}_7$ for complete oxidation of products ?
 (a) SO_2Cl_2 (b) CaCl_2
 (c) COCl_2 (d) SOCl_2
20. Which of the following can be liquefied most easily?
 (a) He (b) Ne (c) Xe (d) Kr

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. If Y_2 in given reaction is Cl_2 then "X" is/are

$$\text{Y}_2 + 2\text{X}_{(\text{aq})}^- \rightarrow 2\text{Y}_{(\text{aq})}^- + \text{X}_2$$

 (a) F (b) Cl
 (c) Br (d) I

22. Hydrogen sulphide exhibits
 (a) acidic properties
 (b) oxidising properties
 (c) reducing properties
 (d) basic properties.
23. Which of the following gives no residue on heating ?
 (a) NH_4NO_3 (b) NH_4NO_2
 (c) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (d) NH_4Cl
24. Which of the following is paramagnetic ?
 (a) $[\text{Fe}(\text{CN})_6]^{4-}$ (b) $[\text{Ni}(\text{CN})_4]^{2-}$
 (c) $[\text{Ni}(\text{CO})_4]$ (d) $[\text{CoF}_6]^{3-}$
25. Which of the following are coloured ?
 (a) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (b) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
 (c) $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (d) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

The overall decrease in atomic and ionic radii from lanthanum to lutetium (the lanthanoid contraction) is a unique feature in the chemistry of the lanthanoids. It has far reaching consequences in the chemistry of the third transition series of the elements. The decrease in atomic radii is not quite regular as it is regular in M^{3+} ions.

26. Which one of the following oxidising agent is not used for oxidation of potassium manganate to potassium permanganate ?
 (a) CO_2 (b) Cl_2 (c) O_3 (d) H_2O_2
27. Identify P and Q products in given reactions.

$$\text{KI} + \text{MnO}_4^- \xrightarrow{\text{H}^+} \text{P} + \text{Mn}^{2+}$$

$$\text{KI} + \text{MnO}_4^- \xrightarrow{\text{OH}^-} \text{IO}_3^- + \text{Q}$$

 (a) IO_3^- , MnO_2 respectively
 (b) I_2 , Mn^{2+} respectively
 (c) IO_3^- , Mn^{2+} respectively
 (d) I_2 , MnO_2 respectively
28. In acidic medium KMnO_4 oxidises FeSO_4 solution. Which of the following statements is correct?
 (a) 10 mL of 1 N KMnO_4 solution oxidises 10 mL of 5 N FeSO_4 solution.

- (b) 10 mL of 1 M KMnO_4 solution oxidises 10 mL of 5 N FeSO_4 solution.
 (c) 10 mL of 1 M KMnO_4 solution oxidises 10 mL of 1 M FeSO_4 solution.
 (d) 10 mL of 1 N KMnO_4 solution oxidises 10 mL of 0.1 M FeSO_4 solution.

Paragraph for Questions 29 to 31

When two different halogens react with each other, interhalogen compounds are formed. They can be assigned general compositions as XX' , XX'_3 , XX'_5 and XX'_7 where X is halogen of larger size and X' of smaller size and X is more electropositive than X' . As the ratio between radii of X and X' increases, the number of atoms per molecule also increases.

29. The T-shaped interhalogen compound is
 (a) ClF_3 (b) ICl (c) ClF_5 (d) IF_5
 30. Which of the following is an inter-pseudohalogen (pseudohalogen analogues of interhalogen)?
 (a) HSCN (b) ICN
 (c) BrF_5 (d) C_2N_2
 31. Interhalogen compounds are more reactive than the individual halogen because
 (a) two halogens are present in place of one
 (b) they are more ionic
 (c) their bond energy is less than the bond energy of the halogen molecule
 (d) they carry more energy.

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

32. Match the compounds in List I with their bond angles in List II and select the correct answer using the code given below the lists :

List I	List II
P. H_2O	1. 93.3°
Q. H_2S	2. 90°
R. H_2Se	3. 104.5°
S. H_2Te	4. 91°

P	Q	R	S
(a) 2	4	3	1
(b) 3	1	4	2
(c) 4	2	1	3
(d) 1	3	2	4

33. Match List I with List II and select the correct answer using the code given below the lists :

List I	List II
P. XeF_4	1. Distorted octahedral
Q. XeF_6	2. Tetrahedral
R. XeO_3	3. Square planar
S. XeO_4	4. Trigonal pyramidal

	P	Q	R	S
(a)	4	1	3	2
(b)	2	3	1	4
(c)	1	4	2	3
(d)	3	1	4	2

34. Match List-I with List-II and select the correct answer using the code given below the lists :

List I	List II
P. Shows maximum oxidation number in $3d$ series	1. Sc
Q. Lowest melting point in $3d$ series	2. Mn
R. Most abundant metal in $3d$ series	3. Zn
S. M^{3+} ion has inert gas like configuration	4. Fe

	P	Q	R	S
(a)	2	1	4	3
(b)	2	3	4	1
(c)	3	2	4	1
(d)	4	3	1	2

SECTION - V

Assertion Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
 (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
 (c) If assertion is true but reason is false.
 (d) If both assertion and reason are false.

35. **Assertion :** Zinc does not show characteristic properties of transition metals.

Reason : In zinc, outermost shell is completely filled.

36. **Assertion :** Vapours produced by the reaction of NaBr and concentrate H_2SO_4 produce white fumes with NH_4OH on glass rod.

Reason : Due to redox reaction Br_2 and SO_2 are formed as a volatile.

37. Assertion : Solubility of noble gases in water increases with increasing size of the noble gas.

Reason : Solubility of noble gases in water is due to dipole dipole interaction.

38. Assertion : Actinoid contraction is greater from element to element than lanthanoid contraction.

Reason : The 5 *f*-electrons themselves provide poor shielding from element to element in the series.

39. Assertion : The S-S-S bond angle in S₈ molecule is 107°.

Reason : S₈ has a V-shape.

40. Assertion : Arsenic (V) chloride is relatively less stable than phosphorus (V) chloride.

Reason : Incomplete shielding of nucleus in arsenic as compared to phosphorus, thereby increasing the energy of 4s orbital in arsenic.

SECTION - VI

Integer Value Correct Type

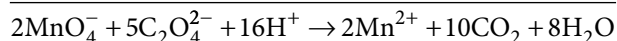
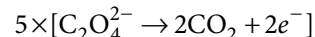
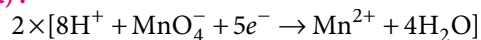
This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. Moles of PH₃ gas produced when 1 mole of calcium phosphide reacts with excess of water is
42. P₄O₁₀ has short and long P—O bonds. The number of short P—O bonds in this compound is
43. Xenon hexafluoride reacts with silica to form a xenon compound X. The oxidation state of Xe in X is
44. The number of lone pairs of electrons present in central atom of ClF₃ is
45. The Gd^{x+} ion has exactly half filled 4*f* subshell. The value of *x* is
46. Titanium shows magnetic moment of 1.73 B.M. in its compound. The oxidation number of Ti in the compound is
47. A greenish yellow gas reacts with an alkali metal hydroxide to form a halate which can be used in fire works safety matches. The halate molecule formed has *x* number of oxygen atoms. The value of *x* is
48. Iron sulphide is heated in air to form A, an oxide of sulphur. A is dissolved in water to give an acid. The basicity of this acid is
49. Total no. of oxygen atoms which are in –1 oxidation state in CrO₅ is
50. The most common oxidation state for selenium in its compounds with oxygen is

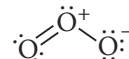
SOLUTIONS

1. (c)

2. (a):



3. (c): O₃ is violet black solid, diamagnetic in nature and has bent structure.



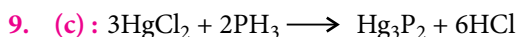
NOCl and ONO[–] have same no. of valence electrons and hence are isoelectronic.

4. (c): Br₂ displaces I₂ from iodide (I[–]) on the starch paper which gives a violet complex of starch-iodine.

5. (d): In case of lanthanoids, the element with *x**f* electrons has a similar colour to that of (14 – *x*) *f* electrons.

6. (c): Xe, Kr and Ar form clathrates. He does not form clathrates as it is too small to be entrapped within the cavities of compounds.

7. (c): Greater the element-element bond strength, higher is the tendency towards catenation. As the size increases from S to Te, the bond dissociation energy decreases. O—O bond energy is however, smaller than that of S—S because of inter electronic repulsions within the small sized oxygen atoms. Thus sulphur has the maximum tendency towards catenation.



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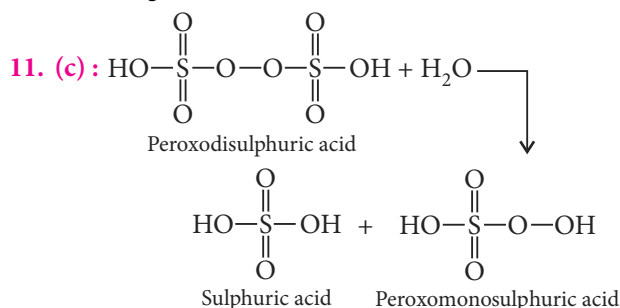
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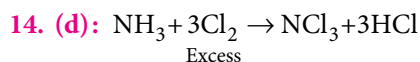
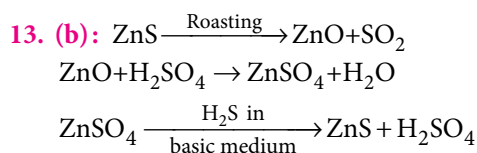
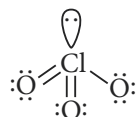
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10. (b): As the electronegativity of X in X_2O decreases from F to Br, the bond pairs of electrons move closer to the central atom (O) and thus bond pair repulsion increases which increases the $X-O-X$ bond angle from F_2O to Br_2O .



12. (a): In ClO_3^- ion, the hybridisation is sp^3 and shape is pyramidal.

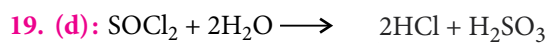


15. (a): As the size of the anion increases from O^{2-} to Te^{2-} their stability decreases. Therefore, O^{2-} is most stable.

16. (d): Sc^{3+} has d^0 configuration hence, it is diamagnetic in nature.

17. (b): Most stable oxidation state of lanthanoids is +3. Thus, the elements which have +4 oxidation state e.g., Ce (IV) act as oxidising agents while the elements with +2 oxidation state e.g., Eu (II) act as reducing agents.

18. (c): Lesser the electronegativity of metal and lower the oxidation state, more is the basic character of oxide or lesser is the acidic character.

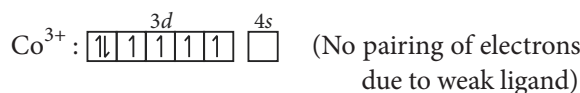
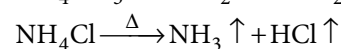
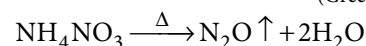
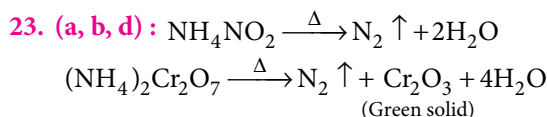
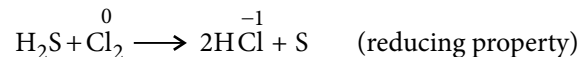
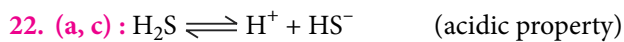


H_2SO_3 is a reducing agent. None of the other produce reducing agent.

20. (c): van der Waals' forces of attraction increase

from He to Xe as the size of their atoms increases. Thus, the ease of liquefaction increases from He to Xe.

21. (c, d): In general, a halogen oxidises halide ions of higher atomic numbers.

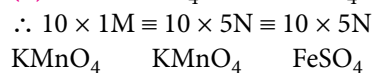
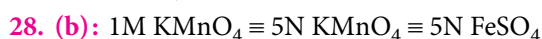


Hence $[\text{CoF}_6]^{3-}$ is paramagnetic.

25. (a, b, c): $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ contains Cu^{2+} (d^9 , one unpaired electron), $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ contains Ni^{2+} (d^8 , two unpaired electrons), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ contains Fe^{2+} (d^6 , four unpaired electrons) and thus, all are coloured. Whereas, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ contains Zn^{2+} (d^{10} , zero unpaired electron) and is colourless.

26. (d): H_2O_2 is a weak oxidising agent and cannot oxidise a strong oxidising agent like K_2MnO_4 .

27. (d): IO_3^- , MnO_2 and I_2 , Mn^{2+} are the products when I^- reacts with MnO_4^- in basic and acidic solutions respectively.



29. (a): ClF_3 where Cl is sp^3d hybridised has a T-shape structure with two lone pairs of electrons on Cl atom.

30. (b): F_2 , Cl_2 , Br_2 and I_2 – Halogen

ICl , ICl_3 , etc. – Inter halogen

CN^- , SCN^- , OCN^- – Pseudohalogen

ICN – Inter-pseudohalogen

31. (c) : The bond energy of interhalogen compounds is less than the bond energy of halogens.

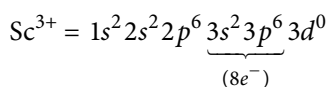
32. (b) : Bond angle of hydrides of group 16 decreases down the group.

33. (d) : XeF_4 is square planar; XeF_6 is distorted octahedral; XeO_3 is trigonal pyramidal and XeO_4 is tetrahedral.

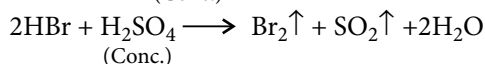
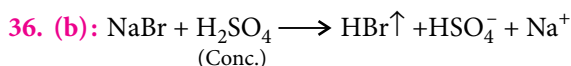
34. (b) : Maximum oxidation number of 3d series is +7 shown by Mn.

Zn have lowest melting point in 3d series.

Fe is the most abundant transition metal in earth crust.



35. (c) : Zinc does not have partly filled d-subshell in its atomic state or its common oxidation state +2.



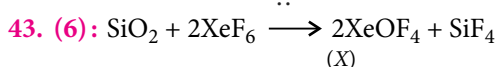
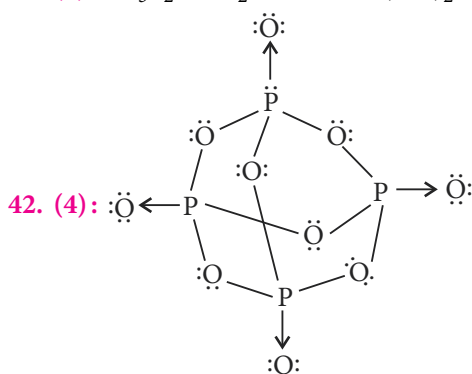
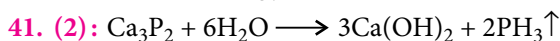
Red-Brown vapours of Br_2 accompanies the hydrogen bromide so that it produces white fumes of NH_4Br with NH_4OH .

37. (c) : Solubility of noble gases in water is due to dipole induced dipole interaction.

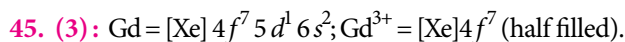
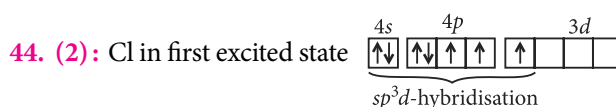
38. (a)

39. (c) : S atoms in S_8 molecule undergo sp^3 -hybridisation and contain two lone pairs of electrons on each.

40. (c) : Incomplete shielding of nucleus in arsenic decreases the energy of 4s.

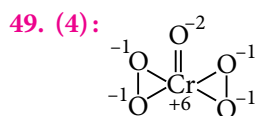
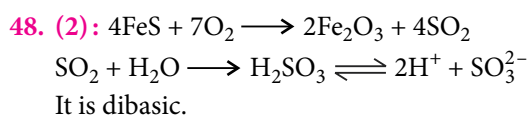


Oxidation state of Xe in (X) is +6.



46. (3) : μ_{eff} value of 1.73 B.M. corresponds to one unpaired electron. $\text{Ti}^{3+} = 3d^1$ ($\text{Ti} = 3d^2 4s^2$).

47. (3) : $3\text{Cl}_2 + 6\text{KOH} \longrightarrow \text{KClO}_3 + 5\text{KCl} + 3\text{H}_2\text{O}$
 KClO_3 is used in fire works and safety matches and Cl_2 is greenish yellow gas.



50. (4) : Selenium shows +4 oxidation state in SeO_2 .

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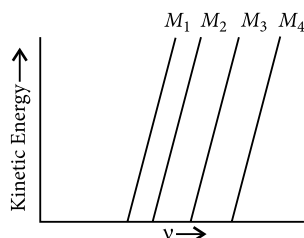
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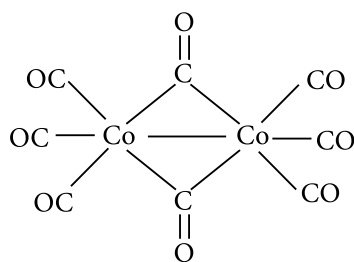
- The pair of amphoteric species is
(a) H_2CO_3 and HCO_3^- (b) H_2CO_3 and H_2O
(c) CO_3^{2-} and H_3O^+ (d) HCO_3^- and H_2O
- On introducing a catalyst at 500 K, the rate of a first order reaction increases by 1.718 times. The activation energy in presence of catalyst is 4.15 kJ mol^{-1} . The slope of the plot of $\ln k$ (in sec^{-1}) vs $1/T$ (T in Kelvin) in absence of catalyst is ($R = 8.3 \text{ J mol}^{-1}\text{K}^{-1}$)
(a) +1 (b) -1
(c) +1000 (d) -1000
- Natural abundances of ^{12}C and ^{13}C isotopes of carbon are 99% and 1%, respectively. Assuming they only contribute to the mol. wt. of C_2F_4 , the percentage of C_2F_4 having a molecular mass of 101 is
(a) 1.98 (b) 98
(c) 0.198 (d) 99
- Isomers which can be interconverted through rotation around a single bond are called
(a) conformers (b) diastereomers
(c) enantiomers (d) positional isomers
- A hypothetical reaction, $\text{A}_{(\text{g})} + \text{B}_{(\text{g})} \rightleftharpoons \text{C}_{(\text{g})} + \text{D}_{(\text{g})}$ occurs in a single step. The specific rate constant of forward reaction at $T\text{K}$ is $2.0 \times 10^{-3} \text{ mol}^{-1} \text{ L s}^{-1}$. When reaction is started with equimolar amounts of A and B, it is found that the concentration of A is twice that of C at equilibrium. The specific rate constant of the backward reaction is
(a) $5.0 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$
(b) $8.0 \times 10^{-3} \text{ mol}^{-1} \text{ L s}^{-1}$
(c) $1.5 \times 10^2 \text{ mol}^{-1} \text{ L s}^{-1}$
(d) none of these
- What are the component values (in terms of $h/2\pi$) of the orbital angular momentum along the Z-direction for a $2p$ electron?
(a) $+\frac{1}{2}, -\frac{1}{2}$ (b) $+\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$
(c) +2, +1, 0, -1, -2 (d) +1, 0, -1
- The enthalpies of neutralisation of HClO_4 and Cl_3CCOOH are -13.5 kcal/g-eq. and -14.7 kcal/g-eq. respectively
When 40 g of solid NaOH is added to a mixture of 1 gram molecule HClO_4 and 1 gram molecule Cl_3CCOOH , sodium perchlorate and sodium trichloroacetate are formed in molar ratio of 3 : 1 then,
(a) ΔH for the reaction of NaOH with the mixture is 6.45 kcal
(b) ΔH for the reaction of NaOH with mixture is 13.8 kcal
(c) after the reaction, total number of moles of HClO_4 and Cl_3CCOOH left are 0.54
(d) after the reaction, the total weight of HClO_4 and Cl_3CCOOH left is 147.75 g and ΔH for the reaction of NaOH with mixture is -13.8 kcal.
- Depending on the reaction involved, titration experiments can be categorised into
(a) neutralisation, complexometric and redox titrations
(b) neutralisation, polymerization and ion exchange titrations
(c) redox titrations, particle size exclusion and precipitation titrations
(d) homogeneous, heterogeneous and phase-transfer titrations.

9. A plot of the kinetic energy ($1/2 mv^2$) of ejected electrons as a function of the frequency (ν) of incident radiation for four alkali metal (M_1, M_2, M_3, M_4) is shown below.

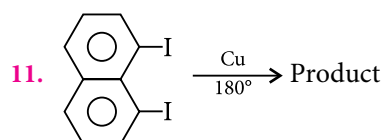


The alkali metals M_1, M_2, M_3 and M_4 are respectively

- (a) Li, Na, K and Rb (b) Rb, K, Na and Li
(c) Na, K, Li, and Rb (d) Rb, Li, Na, and K
10. The oxidation state of cobalt in the following molecule is



- (a) 3 (b) 1
(c) 2 (d) 0



The product is

- (a) (b)
(c) (d) Reaction is not possible.

12. Sanger's reagent is used for the identification of
(a) N-terminal of a peptide chain
(b) C-terminal of a peptide chain
(c) side chain of amino acid
(d) molecular weight of the peptide chain.

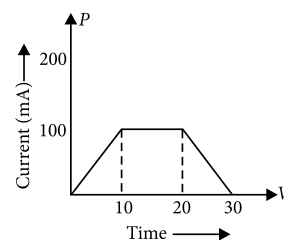
13. In a copper voltameter, mass deposited in 30 sec is 'm' g. If the time current graph is as shown in figure, calculate the electrochemical equivalent of Cu.

(a) $z = m$

(b) $z = \frac{m}{2}$

(c) $z = \frac{m}{5}$

(d) z cannot be calculated from the given data.



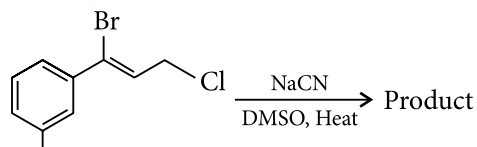
14. In a fcc arrangement of A and B atoms, where A atoms are at the corners of the unit cell, B atoms at the face centers, two atoms are missing from two corners in each unit cell, then the simplest formula of the compound is

- (a) A_7B_6 (b) A_6B_7
(c) A_7B_{24} (d) AB_4

15. The compound X (C_7H_9N) reacts with benzenesulfonyl chloride to give Y ($C_{13}H_{13}NO_2S$) which is insoluble in alkali. The compound X is

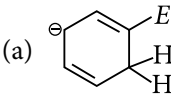
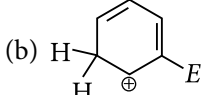
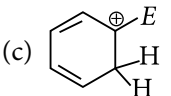
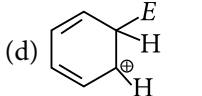
- (a) (b)
(c) (d)

16. The major product formed in the reaction



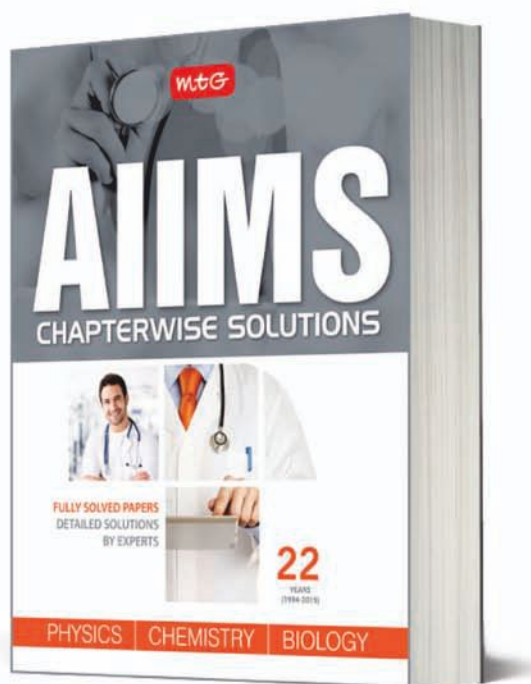
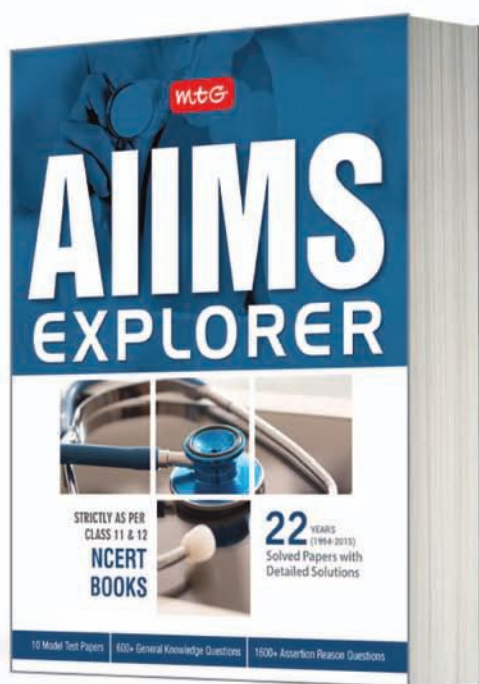
The product is

- (a) (b)
(c) (d)

17. Extraction of silver is achieved by initial complexation of the ore (Argentite) with X followed by reduction with Y. X and Y, respectively, are
 (a) CN^- and Zn (b) CN^- and Cu
 (c) Cl^- and Zn (d) Br^- and Zn
18. By what ratio will the average velocity of the molecules in a gas change when the temperature is raised from 50°C to 200°C ?
 (a) $\frac{1.21}{1}$ (b) $\frac{1.46}{1}$
 (c) $\frac{2}{1}$ (d) $\frac{4}{1}$
19. Which of the following reactions will not produce chlorine gas?
 (a) $\text{K}_2\text{Cr}_2\text{O}_7 + \text{HCl} \xrightarrow{\Delta}$
 (b) $\text{MnO}_2 + \text{HCl} \xrightarrow{\Delta}$
 (c) $\text{KMnO}_4 + \text{HCl} \xrightarrow{\Delta}$
 (d) $\text{K}_2\text{CrO}_7 + \text{H}_2\text{SO}_4 (\text{conc.}) + \text{NaCl} \xrightarrow{\Delta}$
20. The solubilities of K_2SO_4 , BeSO_4 , CaSO_4 and BaSO_4 follow the order
 (a) $\text{K}_2\text{SO}_4 > \text{BaSO}_4 > \text{CaSO}_4 > \text{BeSO}_4$
 (b) $\text{BeSO}_4 < \text{CaSO}_4 > \text{K}_2\text{SO}_4 > \text{BaSO}_4$
 (c) $\text{K}_2\text{SO}_4 > \text{BeSO}_4 > \text{CaSO}_4 > \text{BaSO}_4$
 (d) $\text{BeSO}_4 > \text{K}_2\text{SO}_4 > \text{CaSO}_4 > \text{BaSO}_4$
21. In the benzoin condensation shown
 $2\text{C}_6\text{H}_5\text{CHO} + \text{KCN} \xrightarrow{\text{alcohol}} \text{C}_6\text{H}_5\text{CHOHCOC}_6\text{H}_5$
 the key step is
 (a) the addition of $-\text{CN}$ to carboxyl carbon
 (b) the loss of aldehydic proton
 (c) the self condensation of the two units of aldehyde
 (d) the one when benzaldehyde performs twin functions as donor and acceptor.
22. Two gases A and B present separately in two vessels X and Y at the same temperature with molecular weight M and $2M$ respectively are effused out. The orifice in vessel X is circular while that in Y is a square. If the radius of the circular orifice is equal to that of the length of the square orifice, the ratio of rates of effusion of gas A to that of gas B is
 (a) $\sqrt{2}\pi$ (b) $\sqrt{\frac{\pi}{2}}$
 (c) 2π (d) $\sqrt{\frac{2}{\pi}}$
23. The order of reactivity of K, Mg, Au and Zn with water is
 (a) $\text{K} > \text{Zn} > \text{Mg} > \text{Au}$ (b) $\text{K} > \text{Mg} > \text{Zn} > \text{Au}$
 (c) $\text{K} > \text{Au} > \text{Mg} > \text{Zn}$ (d) $\text{Au} > \text{Zn} > \text{K} > \text{Mg}$
24. In the reaction of benzene with an electrophile E^+ , the structure of the intermediate σ -complex can be represented as
 (a)  (b) 
 (c)  (d) 
25. As indicated by its Lewis structure, which of the following species would probably not exist as a stable molecule?
 (a) CH_3O (b) CH_2O
 (c) C_2H_2 (d) CH_2O_2
26. Point out the correct statement of the following about $\text{Na}_2\text{S}_4\text{O}_6$.
 (a) Average oxidation number of S atom is +2.
 (b) Oxidation number of two S atoms is zero each and that of other two is +5 each.
 (c) Oxidation number of two S atoms is +1 each and that of the other two is +4 each.
 (d) None of these.
27. The H^- ion can be formed in ordinary chemical reaction under proper conditions, but the H^+ ion cannot. The best explanation for this difference is due to
 (a) the radius of the H nucleus
 (b) the electronegativity of H atoms
 (c) the ionisation energy of the H-atom
 (d) the bond dissociation energy of H—H bond.
28. Radicals such as nitric oxide and halogens, lead to the depletion of ozone in the stratosphere. Which of the following represents the decomposition of ozone by any of these?
 (a) $\text{Cl}^\bullet + \text{O}_3 \longrightarrow \text{ClO}^\bullet + \text{O}_2$
 (b) $\text{N}_2\text{O} + 3\text{O}_2 \longrightarrow 2\text{NO}_2 + 3\text{O}_2$
 (c) $\text{HCl} + \text{O}_3 \longrightarrow \text{HClO}_3$
 (d) $(\text{NH}_2)_2\text{CO} + \text{O}_3 \longrightarrow \text{N}_2 + \text{CO}_2 + 2\text{H}_2\text{O}$



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Q1. The intermediates or activated complexes in some reactions exist only for a fraction of second, then how do we detect them?

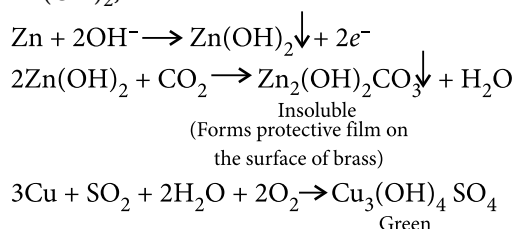
Sandeep Shukla (Kanpur, U.P.)

Ans. Intermediates and activated complexes have sometimes very fleet existence and often survive for only a picosecond. The technique used to observe these particles is femtosecond (10^{-15} second) pulsed lasers. In this experiment, a femtosecond pulse is fired to excite a molecule to a dissociative state. Then, at an interval after the dissociating pulse, a second femtosecond pulse is fired. The frequency of second pulse is set at an absorption of one of the free fragmentation products. Its absorption measures the abundance of this product. These absorption intensity and time delay when plotted over a graph will give a picture about what has happened during the reaction.

Q2. How tamarind (tartaric acid) can clean brass utensils? Give corresponding reactions (if any)?

Swarnabha Choudhury (Howrah, W.B.)

Ans. Brass is an alloy of copper and zinc which gets tarnished and appears dull due to the formation of a layer of its oxide, dirt and grease. Zn is more reactive than Cu, so Zn^{2+} ions are formed which react with the OH^- ions of water to form $\text{Zn}(\text{OH})_2$,



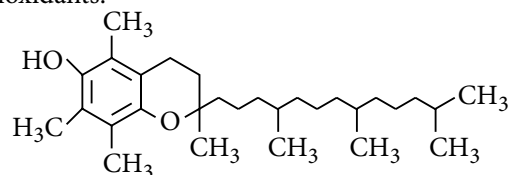
Tartaric acid in tamarind can be efficiently used to clean brass utensils when mixed with soap

solution. Tartaric acid being an acid reacts with basic oxide layer formed on the surface of brass. The soap solution in it cleans the dirt and grease on it. Thus, the cleansing action of tartaric acid is simply an acid base reaction in which tartaric acid reacts with basic oxide to form soluble salts and water molecules, leaving behind a clean surface of brass.

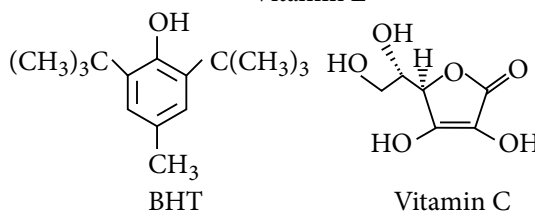
Q3. What are antioxidants and how do they help us to stay healthy?

Pratayaksh Virmani (Chandigarh, Punjab)

Ans. Antioxidants are compounds that inhibit autoxidation by rapidly reacting with peroxy radicals to give stabilised radicals that do not continue the chain reaction of oxidation. Vitamin E (α -tocopherol), vitamin C and BHT (butylated hydroxytoluene) are the examples of antioxidants.



Vitamin E



BHT

Vitamin C

In our body, various peroxy radicals are present which undergo a free radical chain reaction that could cause cell damage. This cell damage may cause early ageing signs like wrinkles etc. Antioxidants react with these peroxy radicals to form stable radical which prevents damage of cells and thus, help us to keep healthy.

Vitamin C is though an antioxidant but, recent studies suggest that supplements over 500 mg per day may have prooxidant effects.

Q4. When perhydrol (H_2O_2) is applied on a wound, bubbles are produced. Please explain why does it happen?

Akila Iyer (Mayur Vihar, New Delhi)

Ans. Bubbles of O_2 are produced due to decomposition of H_2O_2 by an enzyme 'catalase' present in tissues and in blood. This enzyme prevents accumulation of H_2O_2 in the body which could damage tissues.





ADVANCED CHEMISTRY BLOC

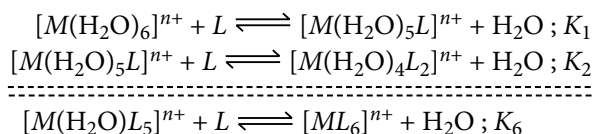
(STABILITY OF COMPLEXES)

Mukul C. Ray, Odisha

Stability simply refers to 'thermodynamic stability' of complexes. Besides this common term, there is another term called 'kinetic stability'. A thermodynamically stable complex may be highly reactive in one particular reaction. Reactivity is linked to activation energy. Only thermodynamic stability is discussed here.

Stability Constants

In aqueous solution, metal ions are well thought out to exist as aqua complexes. In the complexation reaction, the incoming ligand replaces water molecule. Consider a hexa-coordinated aqua complex of metal ion, M^{n+} reacting with neutral ligand, L then the stepwise constants can be written as :



The step-wise constants are equilibrium constants and the overall equilibrium constant is a multiplication of all the above constants. Higher the value of the overall equilibrium constant, more stable is the complex. This is invariably true.

Trend in Stepwise Stability Constants

The stepwise constant values decrease gradually with increasing substitution of water by neutral ligand. This gradual decrease in K value is attributed to three factors, namely, **statistical factor**, **steric factor** and **electrostatic factor**.

As water molecules are gradually replaced by ligand, probability of molecular collision replacing water from the complex decreases. At the beginning, the incoming ligand can replace any one water molecule. So any collision will do but at the last step, only a certain collision, replacing the last left water molecule can form the final complex. This is statistical factor. Steric factor only arises when the ligands are bulkier than the coordinated water molecule. As the crowding around central atom increases, the value of stepwise equilibrium constant gradually decreases. Electrostatic factor appears when the ligand is charged. In the first

step, a ligand replaces a water molecule. Now, when the second ligand with the same charge approaches, it experiences repulsion from the existing ligand. This also contributes to gradual decrease in the value of stepwise equilibrium constant.

Role of Metal Ion

1. In one approach to interpret the stability of the complex, the metal ion is classified. The metal ions are broadly classified into four categories :

- **Category-I (Inert gas configuration type)** : Few metal ions such as Na^+ , Ca^{2+} , Al^{3+} have valence shell configuration as $ns^2 np^6$.
- **Category-II (Pseudo-inert configuration type)** : Here the metal ions have valence shell configuration $ns^2 np^6 nd^{10}$ as is found in Zn^{2+} ($3s^2 3p^6 3d^{10}$), Cd^{2+} , Cu^+ , Hg^{2+} .
- **Category-III (Inert pair configuration type)** : Ions like Sn^{2+} , Pb^{2+} , Tl^+ have general configuration $(n-1)s^2 p^6 d^{10}, ns^2$.
- **Category-IV** : It is an irregular configuration where the valence shell looks like $ns^2 np^6 nd^x$ and $(2+6+x)$ varies between 9 to 17. Ions like Fe^{3+} , Fe^{2+} , Ni^{2+} , Co^{3+} , Cr^{3+} belong to this category.

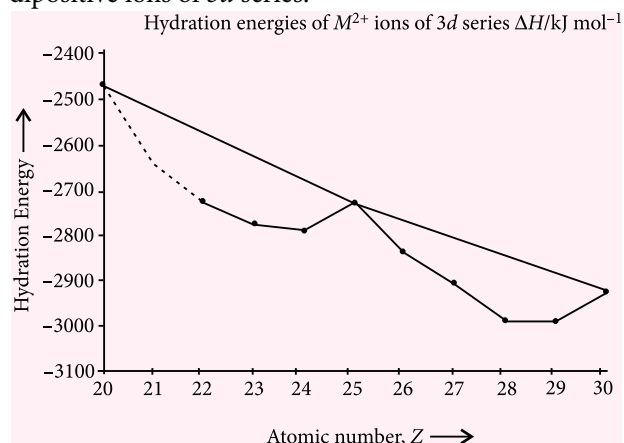
For the first three categories of metal ions stability of complexes is a reflection of the value of ionic potential.

$$\text{Ionic potential} = \frac{\text{Charge}}{\text{Size}}$$

Higher the ionic potential, more stable is the complex. This clearly explains why Li^+ has more complexing ability than Na^+ and why Be^{2+} complexes are more stable than Mg^{2+} . Out of the first three categories, Category-II forms more stable complexes than Category-III which in turn forms more stable complexes than Category-I. The Category-IV metal ions produce the real challenge. The stability of complexes made up of these ions depend on the value of ionic potential, crystal field stabilization energy (CFSE), pairing energy, exchange energy, strength of $M \rightarrow L$ bonding and also strength of $L \rightarrow M$ bonding.

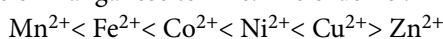
2. There is another approach, which classifies the metal ions as **Class-a** and **Class-b**. The Class-a metal ions are those with high charge density like Na^+ , Li^+ , K^+ , Mg^{2+} , Be^{2+} etc. Such metal ions form complexes of greatest stability with lightest element of groups-VA, VIA and VIIA as donor atoms. Thus, AlF_6^{3-} is more stable than AlCl_6^{3-} . Class-b metal ions include Cu^+ , Ag^+ , Au^+ , Hg^{2+} etc. They form most stable complexes with heaviest element of the above groups. This explains the observed fact that HgI_4^{2-} is more stable than HgCl_4^{2-} .

3. The diagram shows the hydration energies of dipositive ions of 3d series.



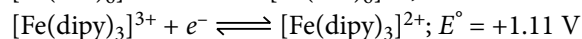
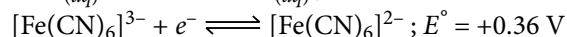
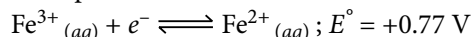
The hydration energy is highest for Cu^{2+} ion. These ions exist as aqua complex in the water solution. The straight line shows the expected value of hydration energy on theoretical grounds. The gradual increase is due to decrease in size of ions. The double humped curve shows the experimental findings. At atomic number 21, the diagram has a broken line, as Sc^{2+} ion does not exist. The observed values agree with the experimental findings at atomic number 20, 25 and 30. As water is a weak field ligand, d^5 has the configuration $t_{2g}^3 e_g^2$ and d^{10} has the configuration $t_{2g}^6 e_g^4$ and these ions do not have any CFSE. For other ions there is contribution of CFSE to hydration energy. Although CFSE accounts only around 5% of the total bonding energy but still it takes the deciding role as other factors almost remain constant. Again, from this discussion it seems as if Ni^{2+} should have the highest hydration energy as it is a d^8 ion but rather Cu^{2+} is found to have the highest, because of a distorted structure, whose reason is beyond the scope of this discussion.

This also explains Irving-William Series that describes the relative stability of complexes made up of dipositive ions of manganese to zinc. The order is :



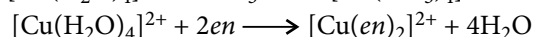
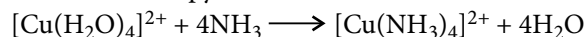
Role of Ligand

1. The negative ligands like CN^- form more stable complexes with ions of high positive oxidation state. On the other hand, neutral pi-acid ligands such as CO, dipyridine form more stable complexes with ions of low positive oxidation state. This idea is used to fine tune electrode potential.



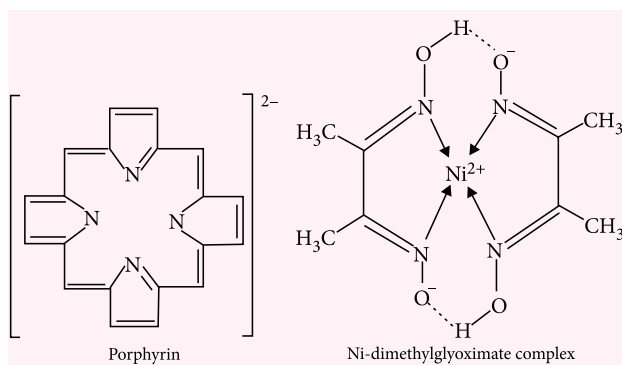
Depending on the relative stability of the complexes, the tendency of formation of complex increases or decreases relative to free metal ions. The more the reduction potential more is the tendency of the equilibrium to move towards right side.

2. Chelating ligands form more stable complex than the non-chelating counter-part. This can be explained by increase in entropy.

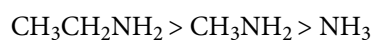


Two molecules of ethylenediamine are consumed and four molecules of water are formed. The value of ΔH is identical for both reactions as donor atoms are identical. It is the positive entropy change of the second reaction which drives the equilibrium towards the product side.

3. Few ligands fairly large in size form complexes of extraordinarily high stability. Example of such ligand is porphyrin which is found in haemoglobin, and chlorophyll. Another example of such complex is Ni-dimethylglyoximate complex which gains high stability due to the effect known as macrocyclic effect.



4. Complex stability also depends on basicity of the ligand. Higher the basicity of the ligand, higher will be the stability of the complex. It has been observed that stability of complexes of Ag^+ from the following ligands decreases in the order





CONCEPT BOOSTER

Dear students!! Hope you all are fine. With my teaching experience for last one decade, I have seen that Inorganic Chemistry especially the Qualitative Analysis has always been a trauma for IIT-JEE aspirants. Shortcut tricks of qualitative analysis are given in this article which will help you a lot to build up the concepts in inorganic chemistry.

Good bye and take care.

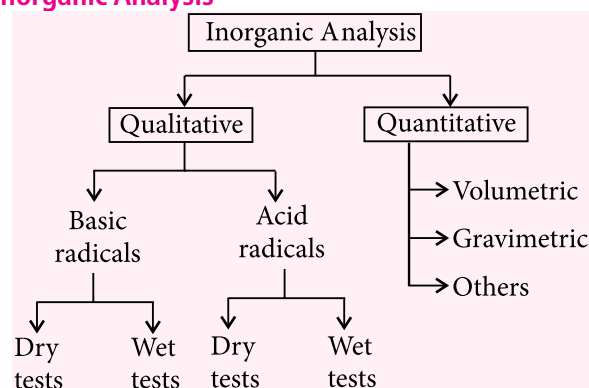
*Arunava Sarkar

QUALITATIVE ANALYSIS

Some Uncommon Reagents

- **Barfoed's reagent** : Dissolve 5 g cupric acetate in 100 mL water containing 1 mL acetic acid.
- **Deniges' reagent** : Dissolve 5 g yellow HgO in 20 mL of concentrated H_2SO_4 . Make up the volume to 100 mL with water.
- **Dragendorff's reagent** : 8 g $\text{Bi}(\text{NO}_3)_3$ in 20 mL solution of mixture of $\text{HNO}_3 : \text{H}_2\text{O} = 1 : 2$ and 27 g KI in 40 mL of water. Mix the solutions with stirring and allow to stand. Separate the deposited crystals of KNO_3 and make up the volume to 100 mL with distilled water.
- **Magnesia mixture** : 55 g $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, 135 g NH_4Cl in 350 mL of liquor NH_3 . Make up the volume to 1000 mL by distilled water.
- **Mayer's reagent** : 13.5 g HgCl_2 , 50 g KI in 940 mL of water.
- **Molisch's reagent** : 10% solution of α -naphthol in alcohol.
- **Reinhardt solution** : Dissolve 67 g $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ in 250 mL of distilled water. Add this solution to the mixture of 133 mL conc. H_2SO_4 and 250 mL of distilled water. Add 133 mL of H_3PO_4 . Make up the volume upto 1000 mL with distilled H_2O .

Inorganic Analysis



Colour of Some Common Inorganic Compounds

Black

- **Sulphides** : Ag_2S , CuS , HgS , PbS , FeS , CoS , NiS , Bi_2S_3
- **Bromide** : CuBr_2
- **Oxides** : CuO , Hg_2O , Fe_3O_4 , MnO_2 , CoO , Ag_2O , NiO
- **Iodide** : NiI_2

Green

- **Oxides** : Cr_2O_3
- **Phosphate** : $\text{CrPO}_4 \cdot 4\text{H}_2\text{O}$

Note :

- All Cr(III) compounds are green except $\text{Cr}(\text{OH})_3$ which is greyish green (gelatinous) and $\text{Cr}_2(\text{CO}_3)_3$ which is grey.
- All Fe(II) compounds are green except FeS which is black.
- All Ni(II) compounds are green except NiO , NiS which are black.

- Carbonate : CuCO_3
- Chloride : $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$
- Hydroxide : $\text{Cu}(\text{OH})_2$
- Iodide : Hg_2I_2

Red

- Oxides : Pb_3O_4 , Cu_2O , HgO , CrO_3 , Fe_2O_3
- Sulphide : As_2S_3
- Complex salt : $\text{K}_3[\text{Fe}(\text{CN})_6]$
- Iodide : HgI_2

Yellow

- Oxides : Bi_2O_3 , Ag_3AsO_3 , $\text{Hg}_3(\text{AsO}_4)_2$, PbO , HgO (sometimes)
- Iodide : AgI , PbI_2 , Hg_2I_2
- Sulphide : CdS , As_2S_3 , SnS_2
- Nitrate : $\text{Hg}_2(\text{NO}_3)_2$
- Complex salt : $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$
- Phosphate : Ag_3PO_4

Note :

- All chromates are in general yellow.
- Ferric compounds are in general yellow.

Brown

- Oxides : Fe_3O_4 , Fe_2O_3 , CdO , PbO_2 , Bi_2O_5
- Sulphides : Bi_2S_3 , SnS
- Hydroxides : $\text{Fe}(\text{OH})_3$
- Chromate : PbCrO_4 (It is actually yellowish brown)
- Arsenic salt : Ag_3AsO_4

Blue

- Complex : Prussian blue
- Copper compounds : Maximum copper compounds except the following :
 $\text{CuCl}_2 \rightarrow \text{Green}$, $\text{Cu}_2\text{O} \rightarrow \text{Red}$, $\text{CuO} \rightarrow \text{Black}$,
 $\text{CuS} \rightarrow \text{Black}$, $\text{CuCrO}_4 \rightarrow \text{Yellow}$
- Cobalt salts : Anhydrous $\text{Co}(\text{II})$ salts

Pink to Purplish -red

- Cobalt compounds (except CoO , CoS which are black)
- Chromium compounds (chrome alum)
- Manganous salts [except oxides of Mn , MnS , $\text{Mn}_3(\text{BO}_3)_2$], permanganates

Add to Your Knowledge

Colour of aqueous and HCl solutions of some ions :

Compounds	Colour in aqueous solution	Colour in HCl solution
Dichromates	Orange	Orange
Chromates	Yellow	Orange
Permanganates	Purple	–
Cobalt(II)	Pink	Blue
Nickel(II), Chromium(III)	Green	Green
Copper(II)	Blue	Bluish green
Manganese(II)	Pale pink	Green
Iron(III)	Yellow	Yellowish brown
Iron(II)	Light green	Green

Note : Aqueous solutions of alkali and alkaline earth salts are colourless unless the anion is coloured.

Identification of Salts

In general, to identify a salt, following steps are followed :

Step-I : Primary Tests

The following primary tests will give an idea that what the salt can be :

- Some common physical appearances
- Dry heating test
- Charcoal cavity test and (if possible) cobalt nitrate test (only after performing the charcoal cavity test)
- Flame test
- Borax bead test
- Dilute H_2SO_4 test
- KMnO_4 test
- Concentrated H_2SO_4 test

Some Common Physical Appearances :

- **Colour :** The first thing which comes under this category is the colour of the salt.

Colours of different salts based on their basic radicals

Basic radical	Carbonate	Sulphate	Sulphide	Nitrate	Chloride
Cu^{2+}	Green dust	Blue crystal	Black dust	Blue crystal	Green crystal
Fe^{2+}	-	Faded green crystal	Black dust	Light green crystal	Light green crystal
Fe^{3+}	-	Yellow crystal	Black dust	Yellow crystal	Yellow crystal
Al^{3+}	-	White crystal	-	White crystal	White crystal
Zn^{2+}	White dust	White crystal	White dust	White crystal	White crystal
Ca^{2+}	White dust	White crystal	White dust	White crystal	White crystal
Mg^{2+}	White dust	White crystal	White dust	White crystal	White crystal
Pb^{2+}	White dust	White crystal	Black dust	White crystal	White crystal

In addition to this, remember the following points :

- ❑ Pink or violet $\rightarrow \text{Co}^{2+}$
- ❑ Light pink (flesh colour) or dull earthy colour $\rightarrow \text{Mn}^{2+}$
- ❑ Dark brown $\rightarrow \text{Fe}^{3+}$
- **Smell** : Take a pinch of salt on your palm, add a drop of water and rub it. If
 - ❑ Vinegar like smell $\rightarrow \text{CH}_3\text{COO}^-$
 - ❑ Smell of ammonia $\rightarrow \text{NH}_4^+$
 - ❑ Rotten egg smell $\rightarrow \text{S}^{2-}$
- **Weight or density of the salt** : This is not a very good observation as the experiment is done with a pinch of salt only.
 - ❑ Heavy salt \rightarrow either Pb^{2+} or Ba^{2+}
 - ❑ Light and fluffy like feather \rightarrow mostly carbonate salts
- **Nature of salt** : If the salt is deliquescent and on absorbing moisture it becomes or takes the form of a paste then it can be any of the following :
 - ❑ If it is a coloured salt then it may be $\text{Cu}(\text{NO}_3)_2$ or FeCl_3 .
 - ❑ However, if the salt is colourless then it can be $\text{Zn}(\text{NO}_3)_2$ or ZnCl_2 or MgCl_2 .

Dry Heating Test

In general, the dry heating test of salts is performed in the following manner :

Take a little amount of salt in the test tube in such a way that no part of the salt sticks to the sides of the test tube *i.e.*, adheres to the sides of the test tube. At first, the tube is heated gently, then strongly. Observe and note down the changes carefully :

	Observations		Inferences
(a) Substances change colour			
(i)	Yellow to brown when hot and yellow when cold	(i)	Pb salts
(ii)	Yellow when hot and white when cold	(ii)	Zn salts
(iii)	Yellowish brown when hot and yellow when cold	(iii)	SiO_2 , Bi_2O_3
(iv)	Residue turns black	(iv)	Cu, Ni, Co, Mn salts
(v)	Yellow to reddish brown or orange	(v)	Sb, Cd and Bi salts

(vi)	Brown to black when hot, brown when cold	(vi)	Fe salts
(vii)	Green	(vii)	Cr salts
(b) A gas or vapour is evolved with characteristic smell and/or colour			
(i)	Droplets of water deposited at the cooler part of the test tube	(i)	Compounds with water of crystallisation
(ii)	Greenish yellow gas with pungent smell, turns starch iodide paper blue	(ii)	Chloride
(iii)	Violet vapours condensing to black crystals	(iii)	Heavy metal iodide <i>i.e.</i> , PbI_2
(iv)	Brown gas	(iv)	Nitrite, nitrate or bromide of heavy metals
(v)	SO_2 gas with smell of burnt sulphur turning acidified $\text{K}_2\text{Cr}_2\text{O}_7$ paper green	(v)	Sulphite, thiosulphate
(vi)	H_2S gas with smell of rotten egg turning lead acetate paper black	(vi)	Sulphide
(vii)	NH_3 gas with characteristic pungent odour turning mercurous nitrate black	(vii)	NH_4^+ salts
(viii)	CO_2 gas turning clear lime water milky	(viii)	Carbonate, bicarbonate
(c)	Colourless melts on heating but solidifies on cooling	(c)	Alkali and alkaline earth metal salts
(d)	Swells on heating with the deposition of droplets of water at the cooler part of the test tube	(d)	Borax and alum

(e)	Original colour white, remains unchanged on heating	(e)	Al and all alkali and alkaline earth metal salts
(f) A sublimate is formed			
(i)	White sublimate formed on the cooler part of the test tube	(i)	As ₂ O ₃ , Sb ₂ O ₃ , NH ₄ ⁺ halides, Hg-salts
(ii)	White sublimate changes to black when exposed to H ₂ S	(ii)	Hg-salts
(iii)	White sublimate changes to yellow when exposed to H ₂ S	(iii)	As ₂ O ₃
(iv)	White sublimate, changes to orange when exposed to H ₂ S	(iv)	Sb ₂ O ₃
(v)	White sublimate with pungent smell of NH ₃ , no change of colour with H ₂ S	(v)	NH ₄ ⁺ salts
(g) Coloured sublimate is formed			
(i)	Black sublimate turns red on prolonged rubbing with a glass rod	(i)	HgS
(ii)	Yellow or yellowish red turns red on rubbing with a glass rod	(ii)	HgI ₂ or a mixture of HgO + KI
(iii)	Grey globules of Hg on rubbing with a glass rod	(iii)	HgO, Hg(NO ₃) ₂ , Hg ₂ (NO ₃) ₂
(iv)	Yellow sublimate	(iv)	As ₂ S ₃ , Sb ₂ S ₃ (sulphur from thiosulphate)
(v)	Orange sublimate	(v)	Sb ₂ S ₃
(vi)	Black mirror with garlic smell	(vi)	As set free from its salts, AsO ₃ ³⁻
(vii)	Violet vapours condensed to blue-black sublimate	(vii)	Iodine set free from its salts

Concept Corner

○ Solubility of halides :

- ❑ Insoluble halides for sure are of Ag, Pb, Hg⁺ and Cu⁺.
- ❑ Order of solubility becomes as
- ❑ Fluoride > Chloride > Bromide > Iodide
- ❑ All the halides of Ca are soluble except CaF₂.

○ Solubility of nitrates and nitrites :

All the metal nitrates and nitrites are water soluble.

○ Solubility of sulphates :

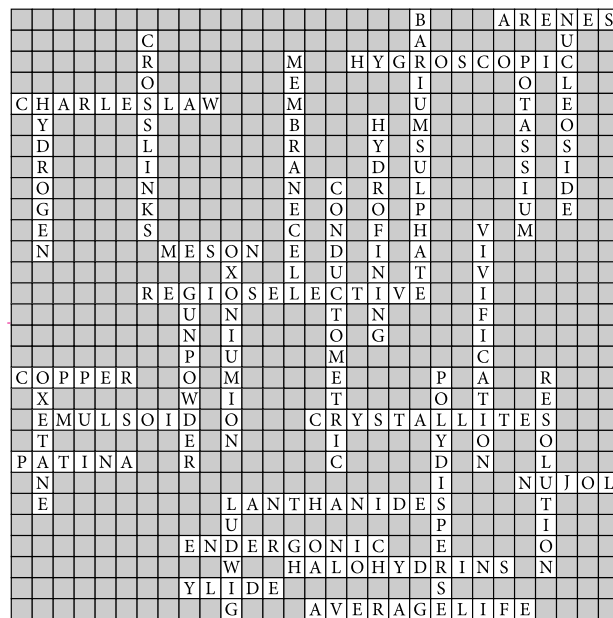
All the sulphates except Pb, Ba, Sr are water soluble. CaSO₄ is sparingly soluble.

List of some common insoluble salts :

Colour of the salt	Insoluble salts with the same colour
1. White	1. CaF ₂ , BaSO ₄ , SrSO ₄ , PbSO ₄ , AgCl, SnO ₂ , SiO ₂ , Sb ₂ O ₃ , Al ₂ O ₃
2. Black	2. HgS
3. Red	3. Fe ₂ O ₃
4. Yellow	4. PbCrO ₄ , AgBr, AgI
5. Green	5. Cr ₂ O ₃ , Cr ₂ (SO ₄) ₃
6. Violet	6. CrCl ₃

...to be continued on the next issue.

SOLUTIONS TO SEPTEMBER 2015 CROSSWORD



Winners of September 2015 Crossword

- Rishi Pathania (Maharashtra)
- Aditi Mukherjee (Pune)

CHEMISTRY MUSING

SOLUTION SET 26

1. (a): $E_1 = E^\circ - \frac{0.059}{1} \log[H^+]_1$

$\therefore E_2 = E^\circ - \frac{0.059}{1} \log[H^+]_2$

On adding (also $E^\circ_{H_2} = 0$)

$$E_1 + E_2 = \frac{-0.059}{1} \{\log[H^+]_1 + \log[H^+]_2\}$$

Now, for $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

$$[H^+] = \frac{K_a [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

$$\Rightarrow [H^+]_1 = K_a \times \frac{y}{x} \quad \text{and} \quad [H^+]_2 = K_a \times \frac{x}{y}$$

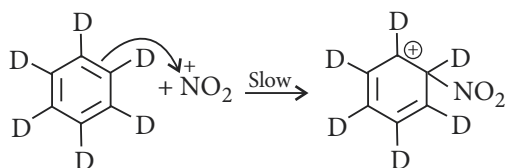
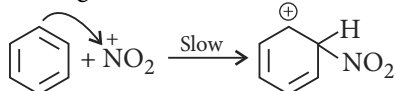
$$\therefore E_1 + E_2 = -\frac{0.059}{1} \left[\log \frac{K_a \cdot y}{x} + \log \frac{K_a \cdot x}{y} \right]$$

$$= -0.059 [2 \log K_a]$$

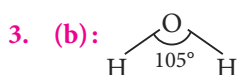
$$\log K_a = \frac{E_1 + E_2}{2 \times (-0.059)} = -\frac{E_1 + E_2}{0.118}$$

or $pK_a = \frac{E_1 + E_2}{0.118}$

2. (c): Electrophilic substitution in benzene is a two step reaction in which the slow step (first step) is common in both the reactions as it does not involve the breaking of C—H or C—D bond.



Had the rate determining step (slow step) involved the cleavage of C—H or C—D bond, nitration of benzene would have been faster than that of hexadeuterated benzene.



$$\therefore \mu_{\text{H}_2\text{O}} = \sqrt{\mu_{\text{OH}}^2 + \mu_{\text{OH}}^2 + 2\mu_{\text{OH}}^2 \cos(105^\circ)}$$

(\because H_2O has two vectors of O—H bonds acting at 105° .)

Let dipole moment of O—H bond be ' a '.

$$\therefore 1.85 = \sqrt{2a^2(1 + \cos 105^\circ)}$$

or a , i.e., $\mu_{\text{OH}} = 1.52$ debye $= 1.52 \times 10^{-18}$ esu cm

Now, $\mu_{\text{O—H}} = \delta \times d$

where, δ is charge on either end

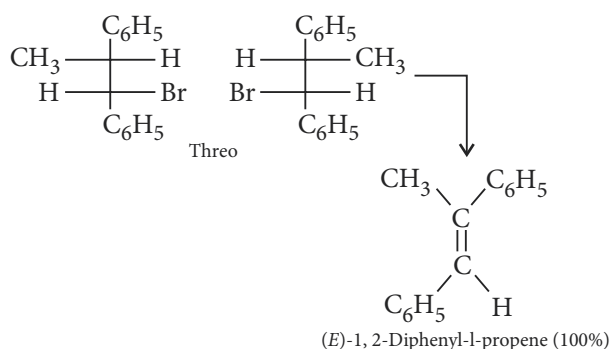
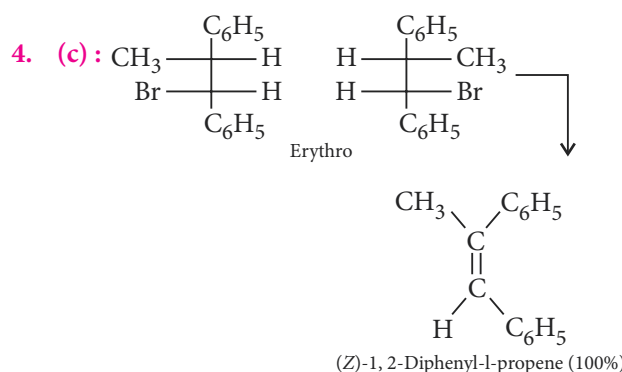
$$\therefore 1.52 \times 10^{-18} = \delta \times 0.94 \times 10^{-8}$$

$$\therefore \delta = 1.617 \times 10^{-10} \text{ esu}$$

Since O acquires 2δ charge, one δ charge from each bond and thus,

$$\text{Charge on O-atom} = 2\delta = 2 \times 1.617 \times 10^{-10}$$

$$= 3.23 \times 10^{-10} \text{ esu}$$



Thus, the reaction is stereoselective as well as stereospecific.

5. (b): Electron in lower energy state move faster. Hence, K.E. increases during transition from higher to lower state.

Solution Senders of Chemistry Musing

SET 26

- Siddharth Roy (WB)
- Devarshi Rawal (Ahmedabad)
- Saurabh Kataria (Ambala)

CROSSWORD



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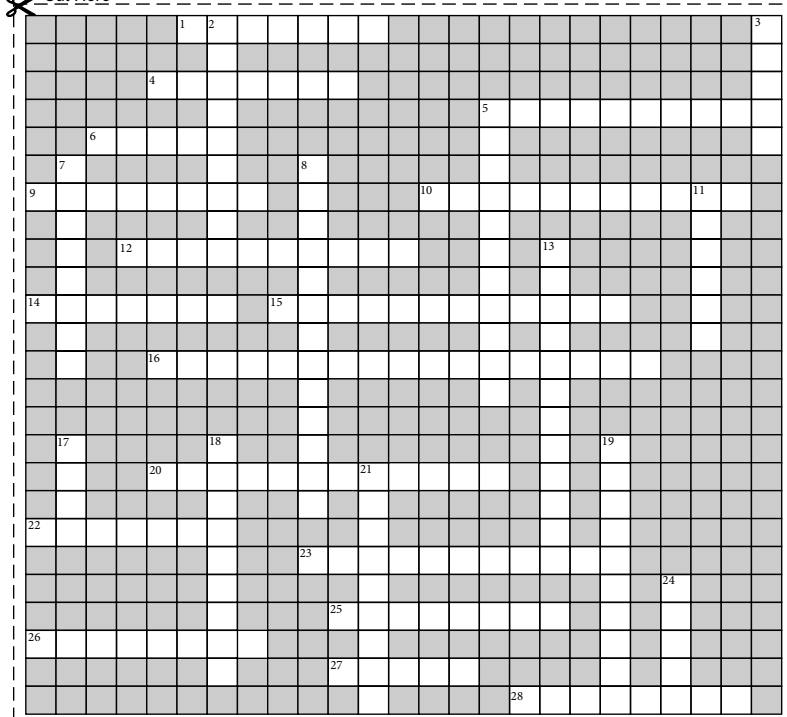
ACROSS

1. Intermolecular cyclic diester formed by alpha hydroxy acids. (7)
4. An inorganic substance used in the dyeing process. (7)
5. The boiling or bubbling of a liquid. (10)
6. IUPAC name of NH_3 . (5)
9. A 40% aqueous solution of formaldehyde which is used to preserve biological specimens. (8)
10. An equimolar mixture of carbon monoxide and nitrogen used as an industrial fuel. (11)
12. The minimum temperature at which sufficient vapours are given off by a flammable liquid to ignite in the presence of spark. (10)
14. A dislocation in a crystal lattice that cannot glide. (7)
15. A method of electrochemical analysis suitable for dilute solutions of those substances which are susceptible to reduction at the mercury cathode. (12)
16. An alternative to sodium fluoride for fluoridising drinking water. (17)
20. The separation of colloidal sol into two liquid phases. (12)
22. Antacid which is used in the treatment of peptic ulcer. (7)
23. Solvents which have greater tendency to accept proton. (11)
25. Element used in xerox type photocopiers to make the photoreceptor to capture the image. (8)
26. Trade name of the mixture of alcohol and ether used as a substitute of petrol. (8)
27. Mixture of iron and copper sulphides obtained in smelting of copper ore. (5)
28. A substance that exhibits the phenomenon of luminescence. (8)

DOWN

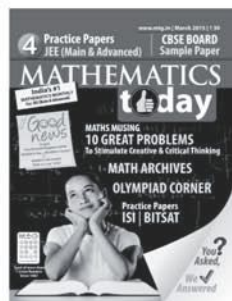
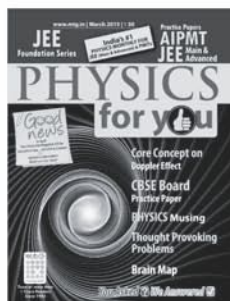
2. The scientist who gave the theory of electrolyte dissociation or ionic theory. (9)
3. Unit of mass which is equal to 10^3 kilograms. (5)

Cut Here



5. The reaction which is always favoured with increase of temperature. (11)
7. Isomers obtained by rotation about single bonds. (8)
8. The process of determining the percentage of alcohol in a given sample. (13)
11. An addition compound that is formed by a reaction in which there is no change in valency. (6)
13. The oil rich in cycloalkanes is known as _____. (12)
17. Monoamide of carbamic acid. (4)
18. The number of contiguous atoms bound to the central atom in a compound. (9)
19. Hygroscopic compounds which can be used for preserving the moisture content of materials. (10)
21. An alloy of aluminium, zinc and copper. (9)
24. The parameter used to express quantitatively the inter electronic repulsion between various energy levels of an atom. (5)

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